PETRUS

ANNETTE

PETRUS-ANNETTE PhD and Early-Stage Researchers Conference 2017

Programme and presentations

Monday 26

14:00 - 18:00

- **Welcome**
  Representatives from PETRUS/ANNETTE organizing committee
- **Lecture of Prof. F.J. Elorza (UPM)**
  Hydro-mechanical and transport processes
- **Lecture of Dr. I. Paiva and Dr. M.J. Reis (IST)**
  Radiation protection issues
- **Lecture of Prof. B. Bazargan Sabet (UL)**
  Front-end nuclear fuel cycle waste

Tuesday 27

9:00 - 18:30

- **PhD/early stage researcher presentations**

------------------------------LUNCH-----------------------------------

- **Lecture of Prof. A. Gens (UPC)**
  Coupled THM analysis for radioactive waste geological disposal
- **Lecture of Prof. J.M. Montel (UL)**
  Natural analogue studies in the geological disposal of radioactive wastes
- **Lecture of Dr. Erika Neeft (COVRA)**
  Carbon-14 Source Term
- **Lecture of Prof. K. Pedersen (Micans)**
  Bacterial life in clay barriers surrounding radioactive waste in geological repositories

CArbon-14 Source Term
CAST

Name: Erika Neeft
Organisation: COVRA (WMO)
Date: 27 June 2017

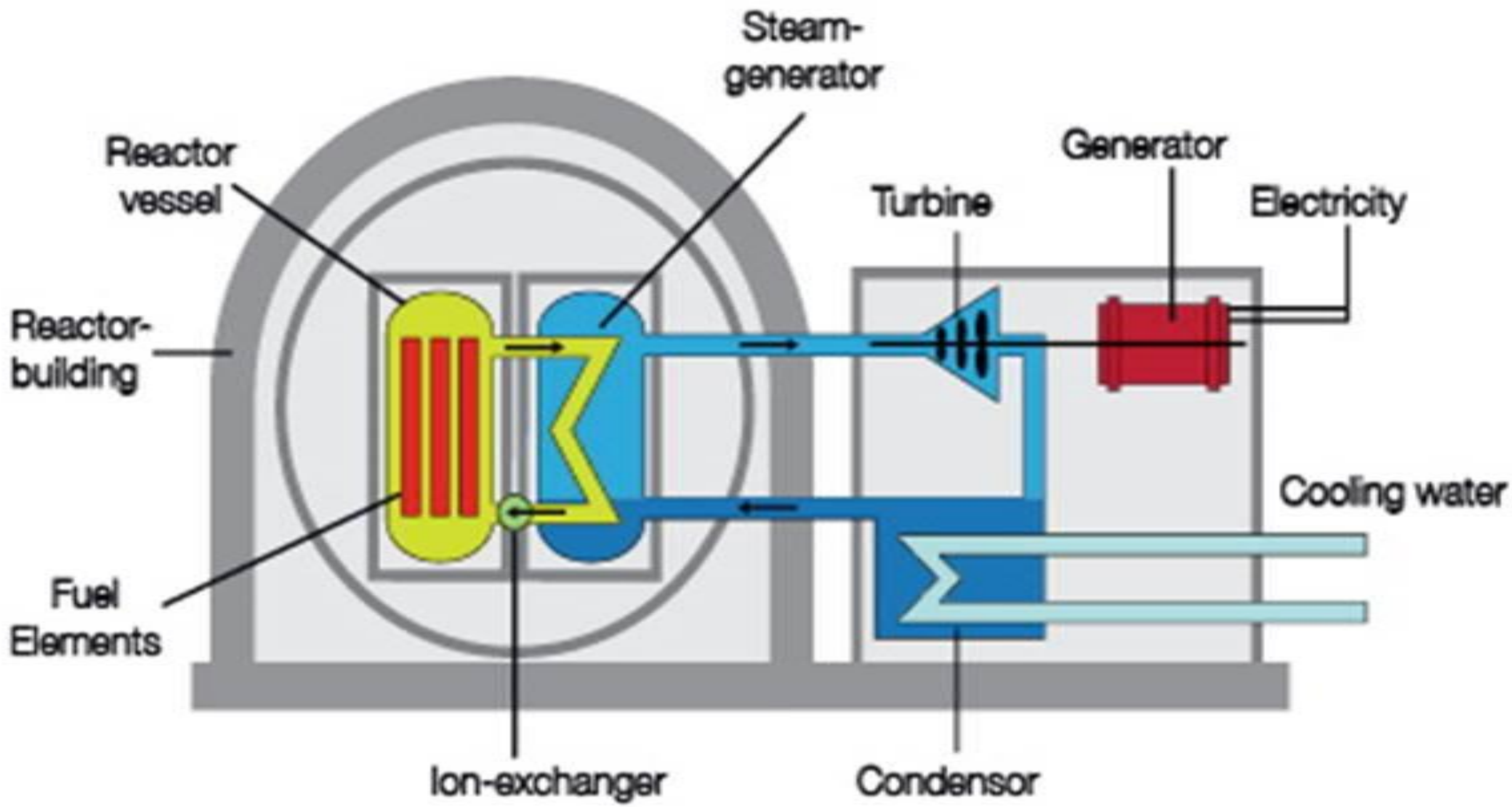
The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project.

Content

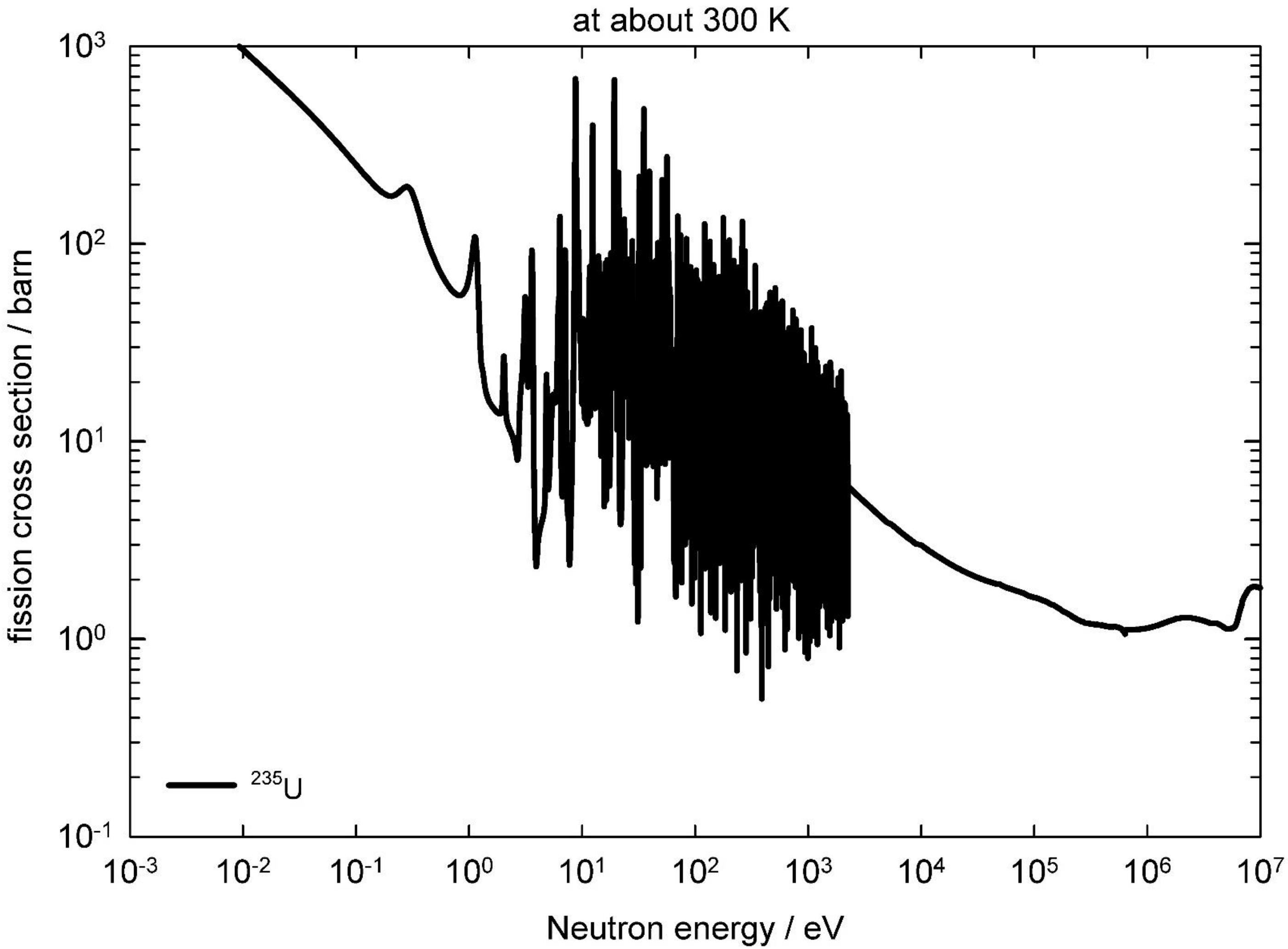
- Radionuclides
  - Generation in a nuclear plant
    - Fission, activation
  - Left for (geological) disposal
    - ETM and DTM
      - carbon-14
        - » Clearance level carbon-14 in waste in EU
- Disposal of waste
  - Potential migration of released radionuclides
    - Gas, dissolved, retarded
    - Natural carbon-14
      - Generation
      - Exposure
    - Potential exposure mechanism artificial carbon-14 if released as gas
  - Carbon-14 Source Term
    - Types of waste investigated
    - Potential release mechanisms at (geological) disposal conditions
      - Cementitious materials

Generation

PWR

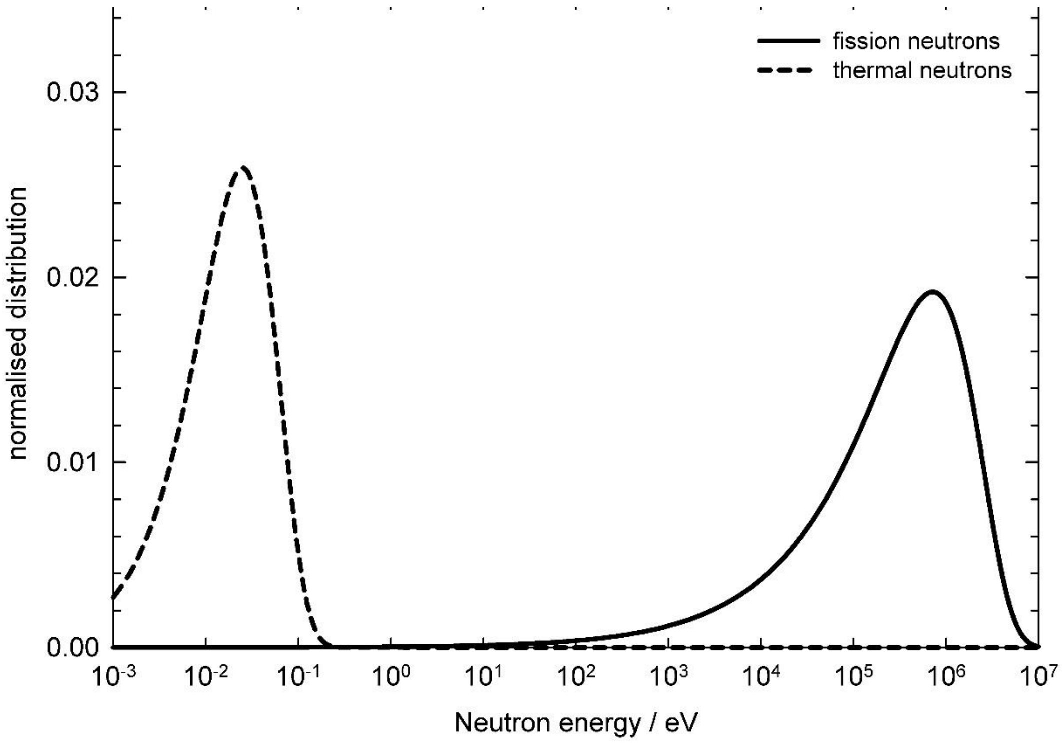


Generation



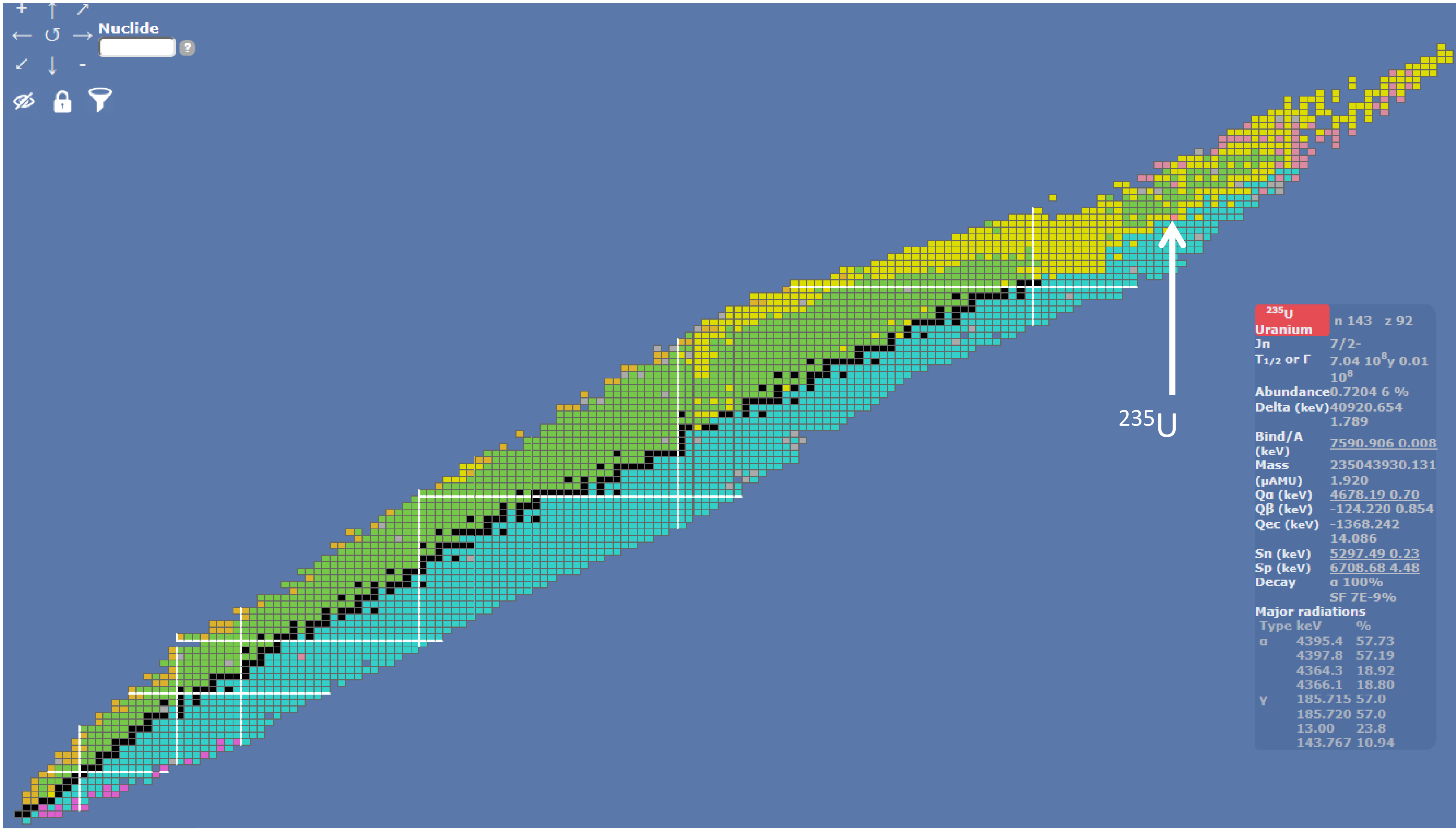
Data from library JEFF3.2 from NEA databank, JANIS, free online

Generation



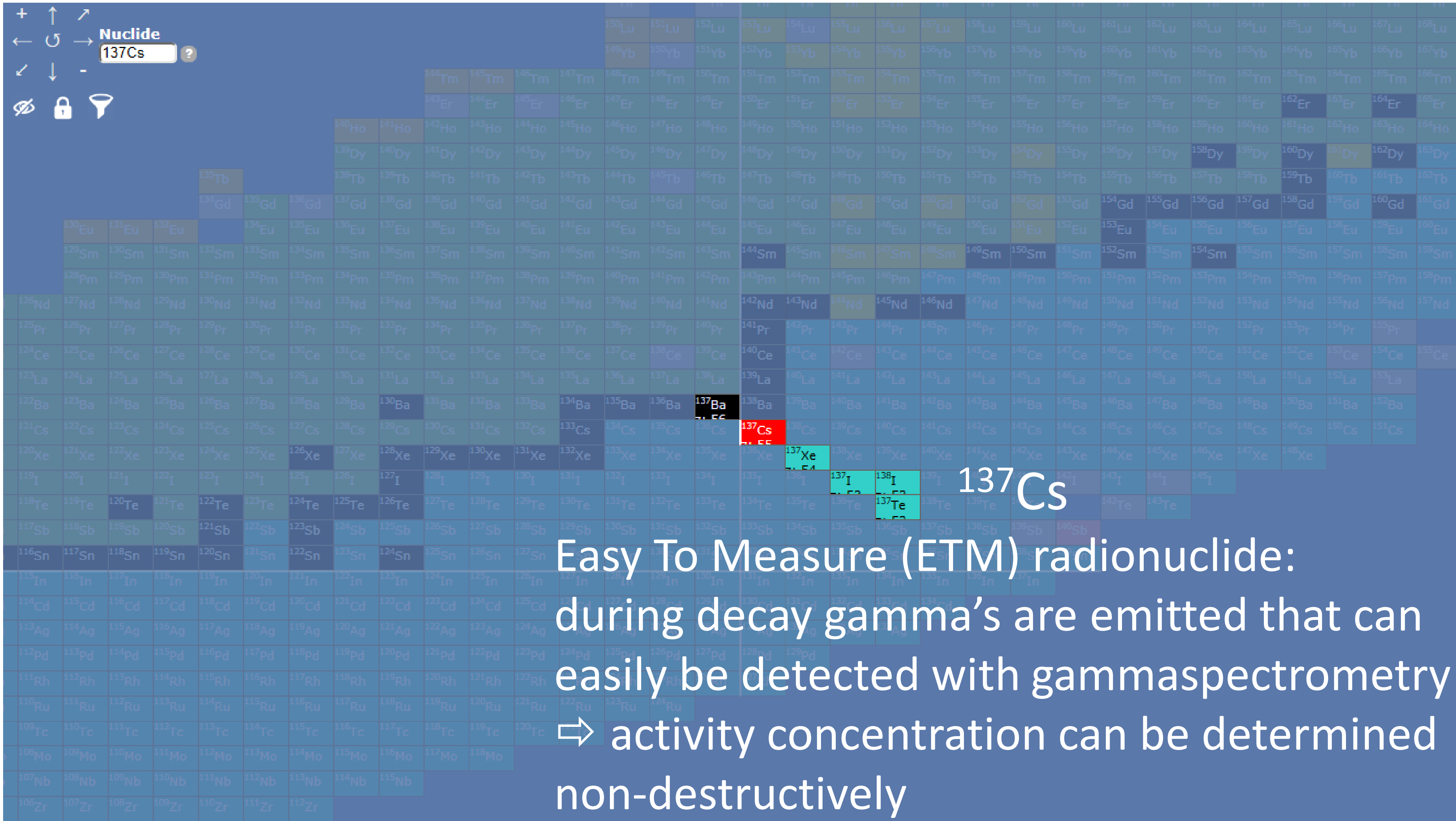
fission neutrons
thermal neutrons
0.03
0.02
0.01
0.00
normalised distribution
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
Neutron energy / eV

Generation



Live chart from IAEA, free online

Example RN left for disposal from decay and fission



Easy To Measure (ETM) radionuclide: during decay gamma's are emitted that can easily be detected with gammaspectrometry ⇨ activity concentration can be determined non-destructively

IAEA

Example RN left for disposal from decay and fission

^{135}Cs

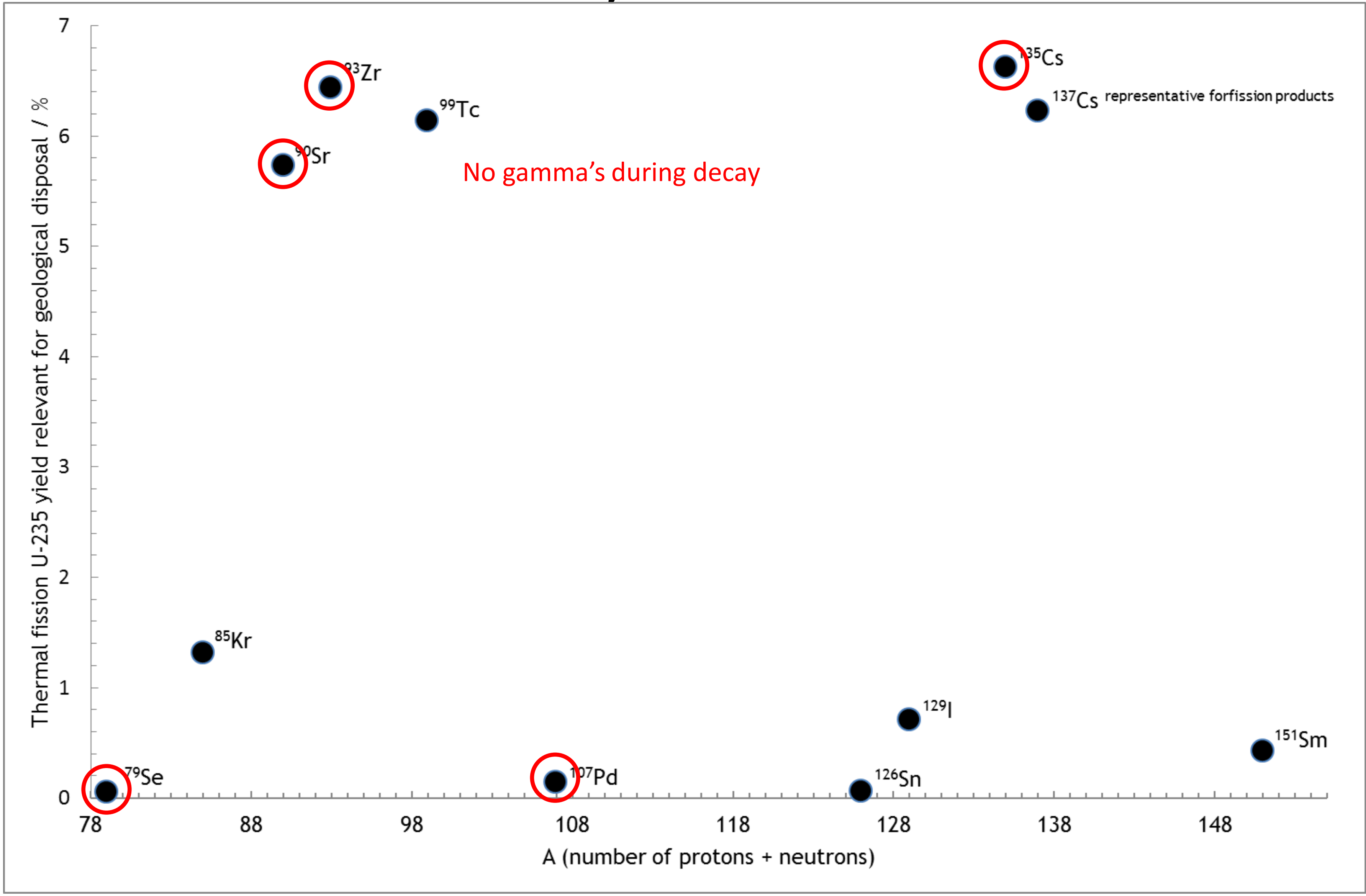
Difficult To Measure (DTM) radionuclide

No emission of gammas during decay ⇨

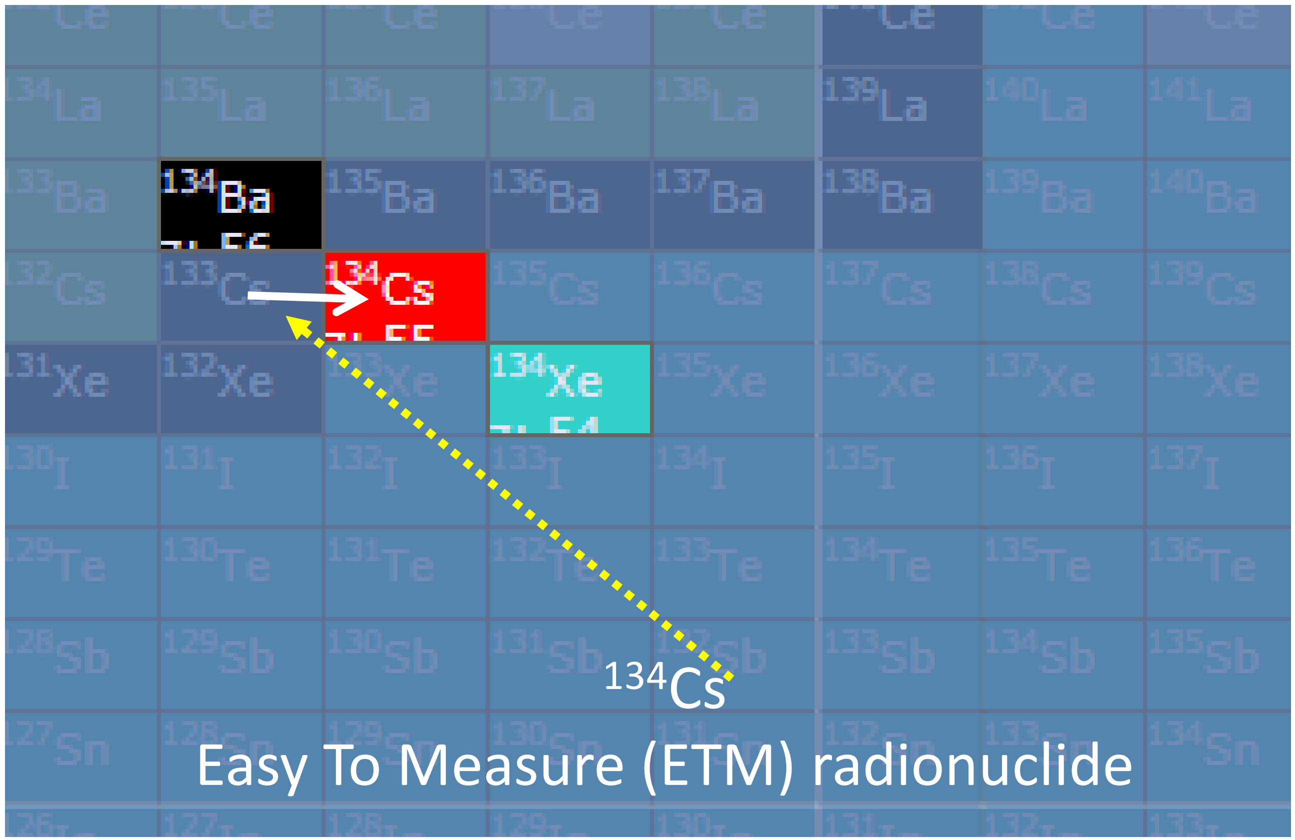
Activity concentration to be measured invasively if needed

IAEA

Examples RN left for disposal from decay and fission

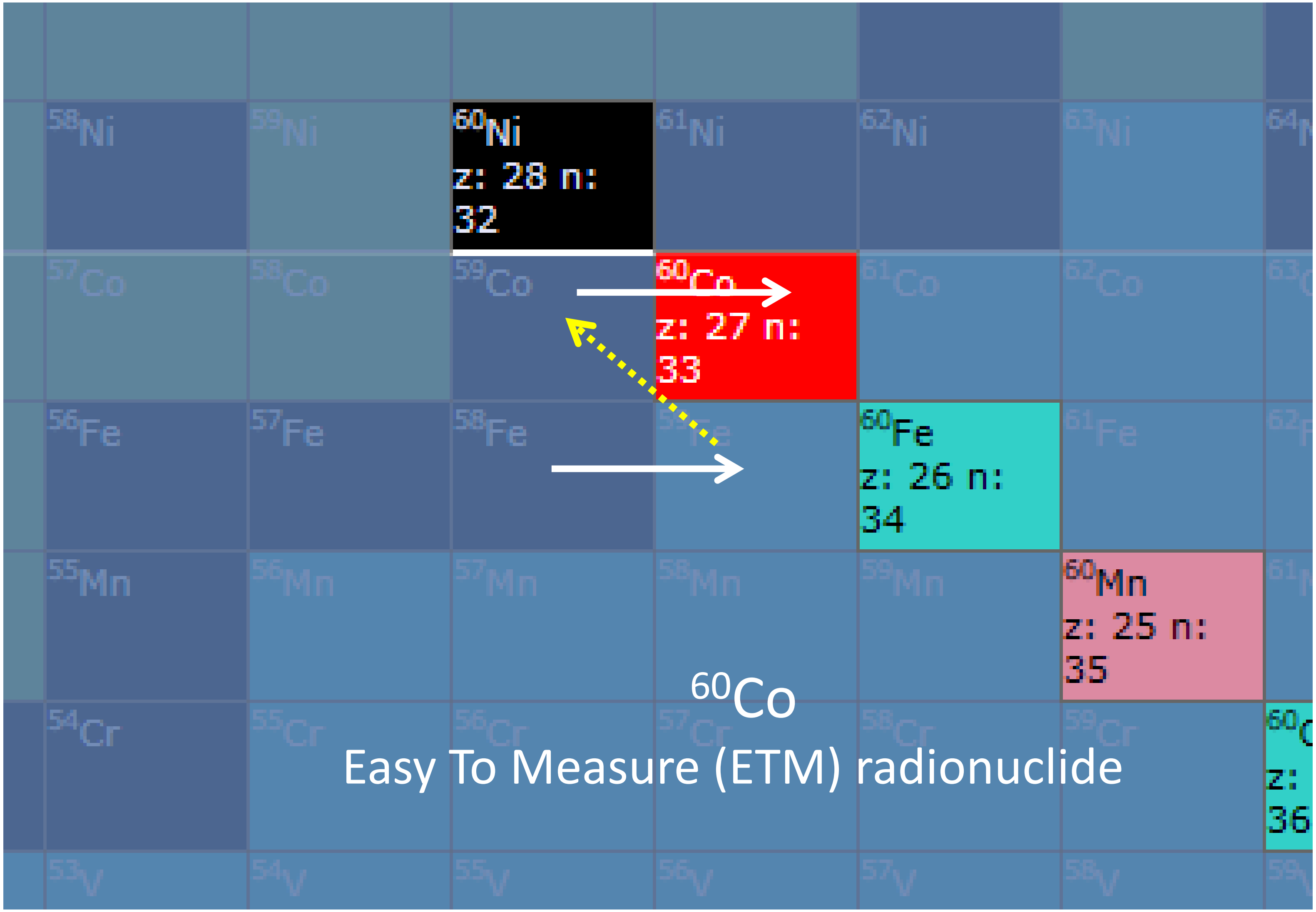


Example RN left
from fission, decay and activation



IAEA

Example RN left perhaps for disposal from activation



IAEA

COVRA's storage period at least 100 years:
Fraction in activity left: $\{^{1}/_{2}\}^{100/t_{0,5}}$ for $^{60}Co=0{,}0000019$
i.e. reduction of a million

Neutron activation

- Identification activation path to obtain the precursors
- Knowledge of the chemical content of precursors
  - Can be impurities

Is RN relevant for disposal?

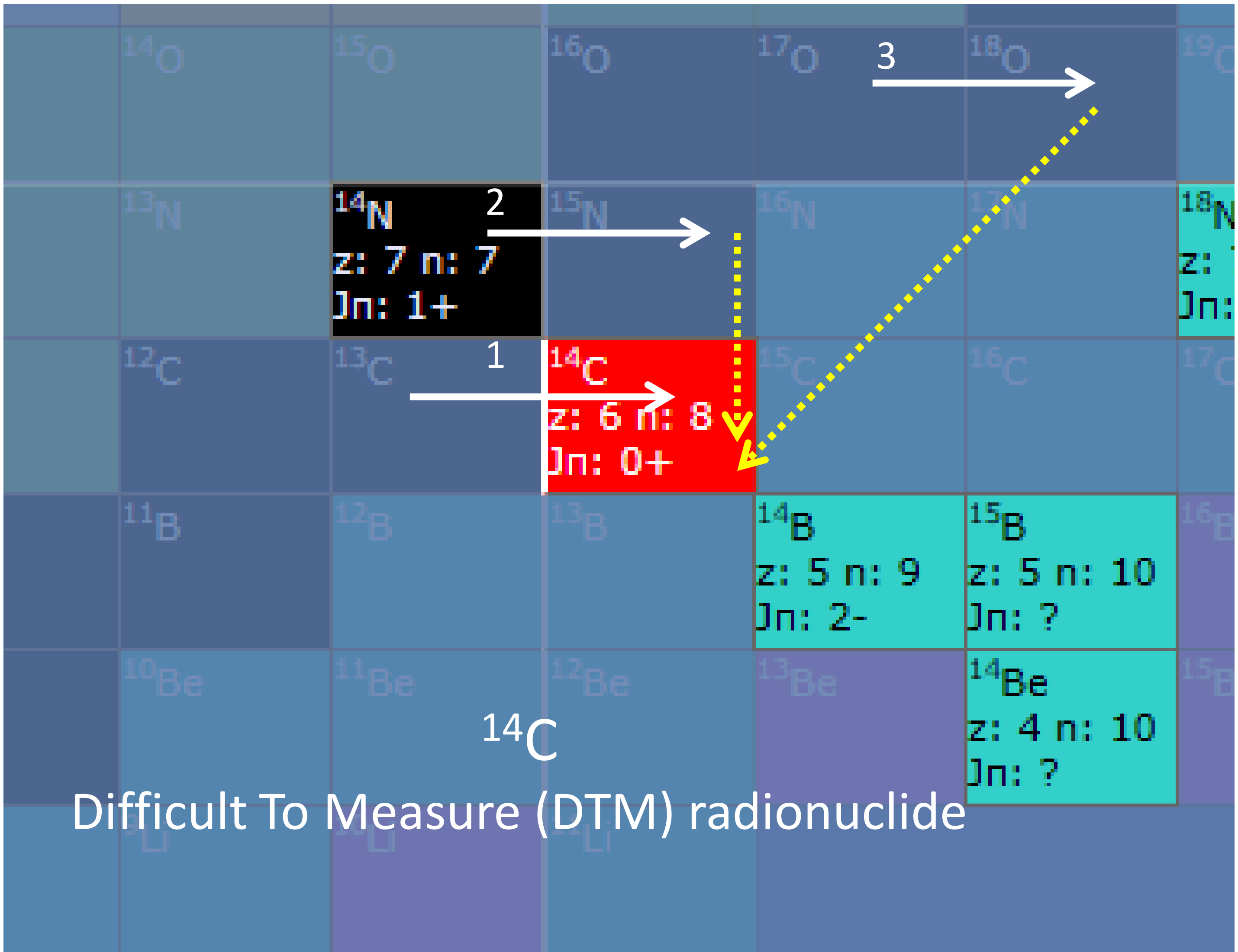
- Clearance levels in EU:
  - Council Directive 2013/59/EURATOM of 5 December 2013 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation, and repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom, Official Journal of the European Union, L13/1-73, 17.1.2014
  - ^{14}C: 1 Bq per gram solid matter for example 0.000024 ppm in iron

COVRA’s storage period at least 100 years:
Fraction in activity left: $\{^1/_2\}^{100/t_{0,5}}$ for ^{14}C=0,99
i.e. no significant reduction after this storage period

A DTM analysis: carbon-14

Bucur, 2015

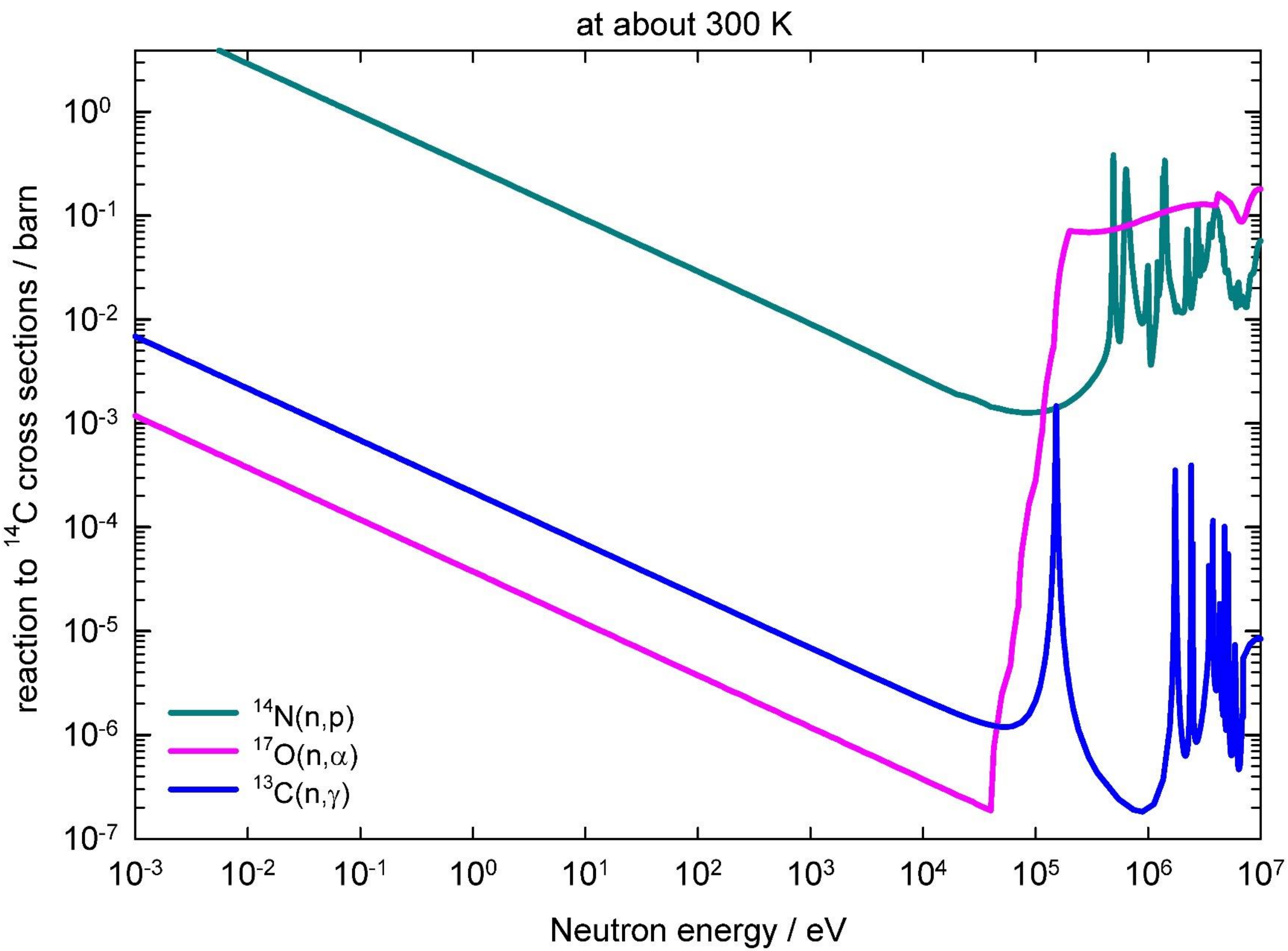
Neutron activation



^{14}C

Difficult To Measure (DTM) radionuclide

Neutron activation

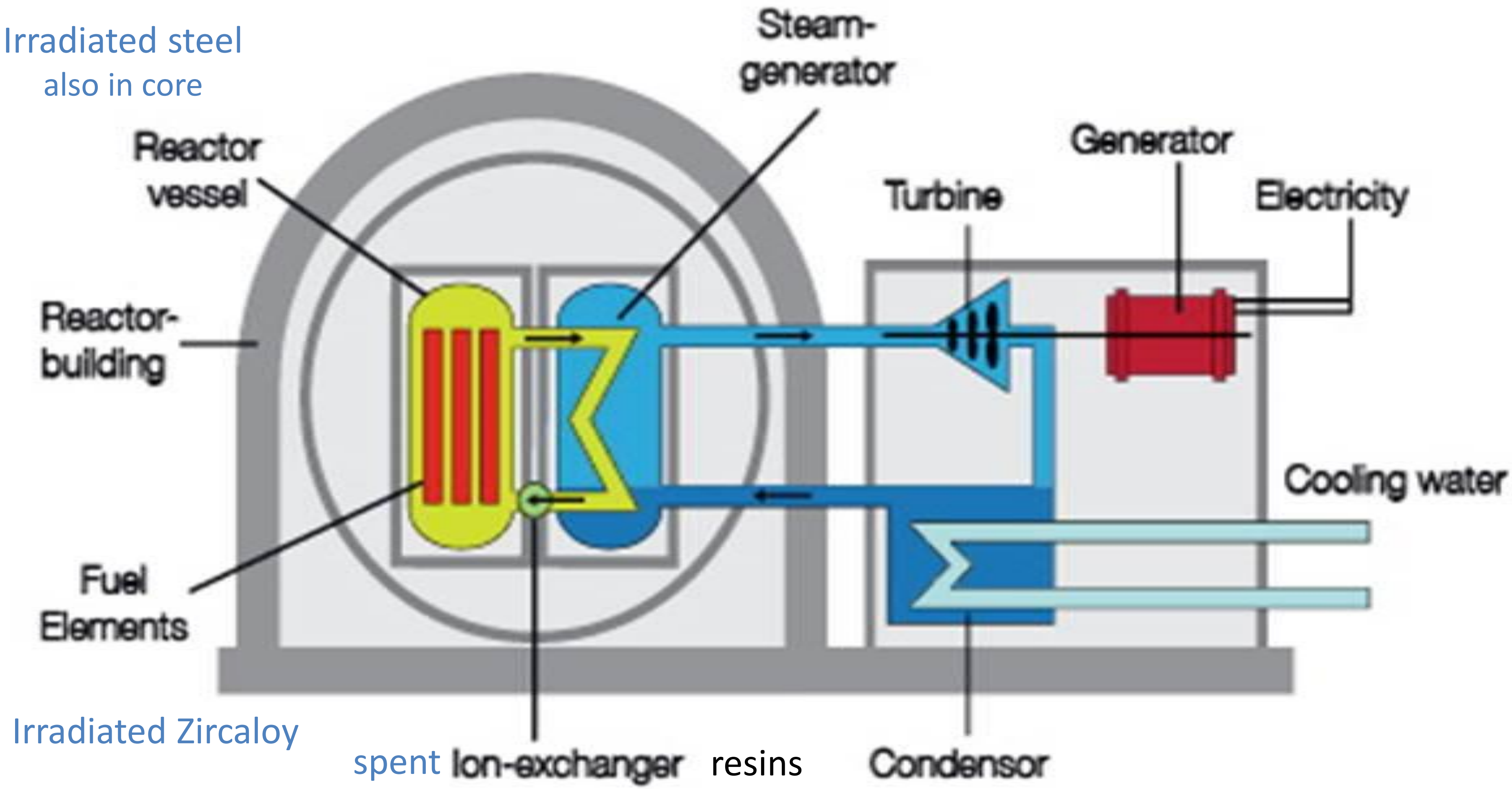


JEFF 3.2 NEA

Neutron activation

- Natural abundances
  - Nitrogen-14 : 99.636%
  - Oxygen-17 : 0.038%
  - Carbon-13 : 1.07%
- Natural abundance + thermal cross sections for the same carbon-14 contribution:
  - Chemical content carbon >> 10^5 chemical nitrogen content
  - Chemical content oxygen >> 10^7 chemical nitrogen content

Types of waste investigated



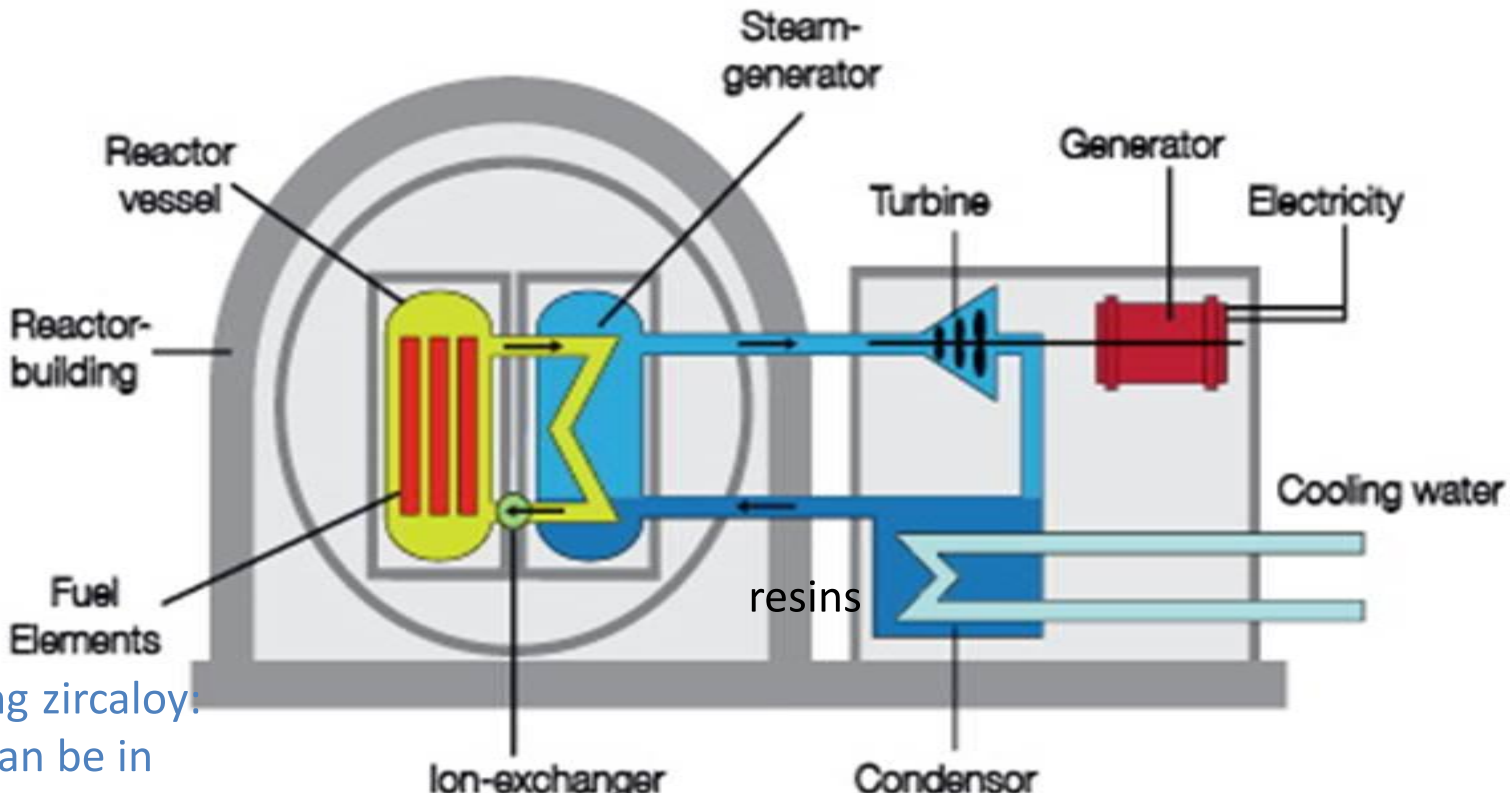
Carbon-14 act.conc.

- Knowledge nitrogen impurities for many types of waste
  - EU study (1984) limit nitrogen impurities
  - IAEA (2004) for example
    - limit air ingress primary coolant
    - pH control primary coolant LiOH instead of hydrazine NH_2-NH_2
- Neutron thermal flux and irradiation period

Bush, 1984; IAEA, 2004

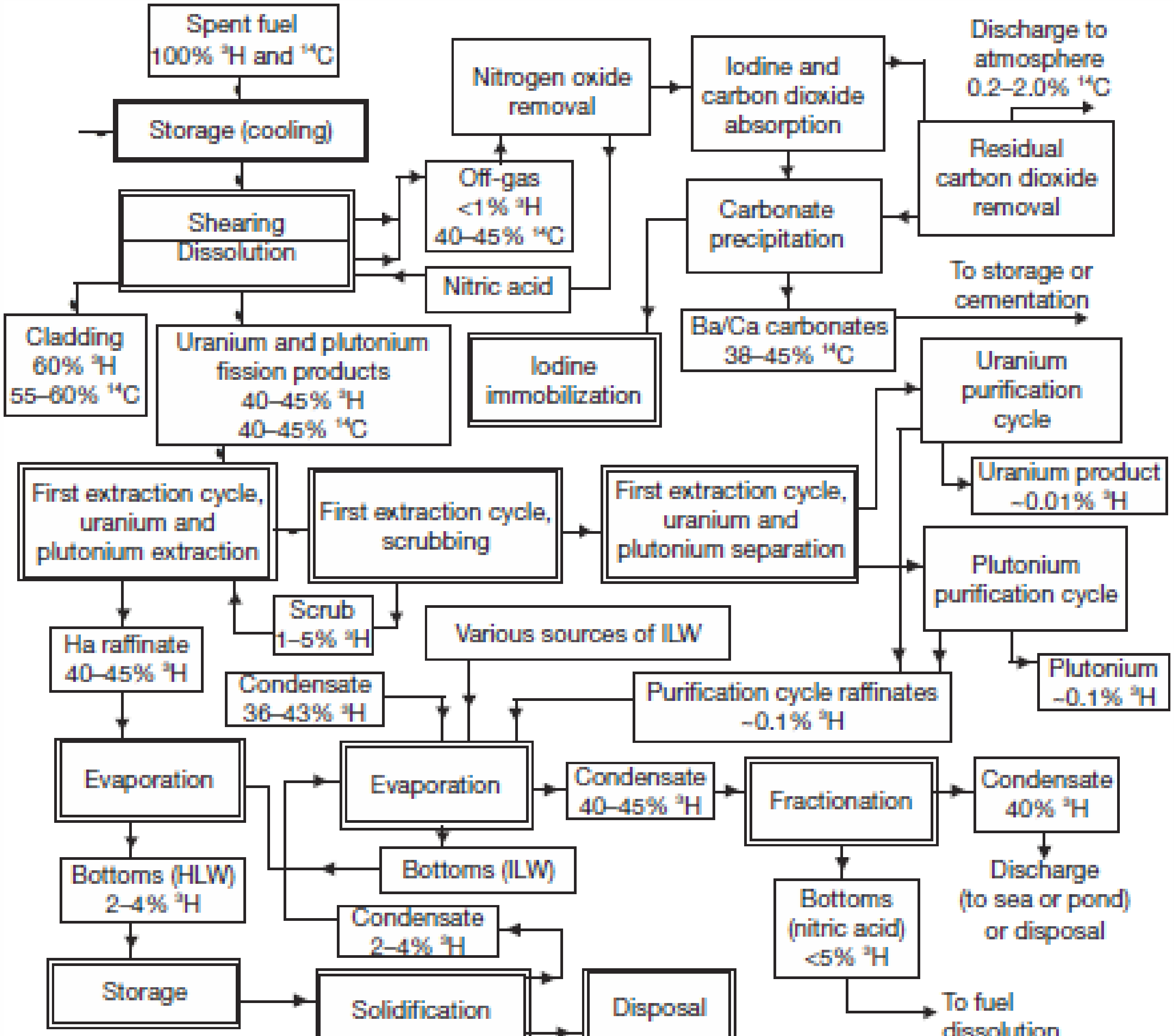
Origin nitrogen

Manufacturing steel: nitrogen can be in
pig iron,
Cokes
Stirring gas
Nitrogen content frequently not reported



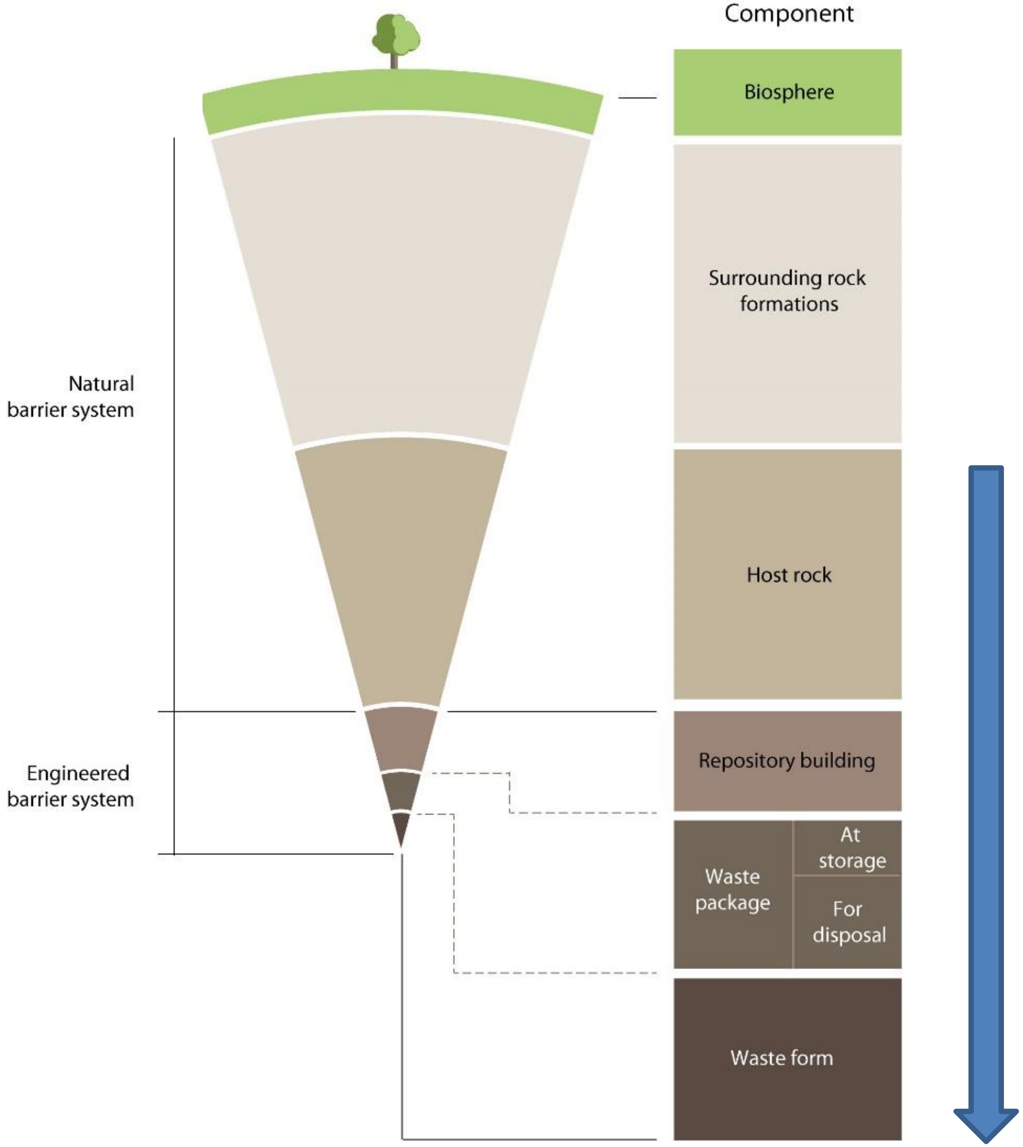
Manufacturing zircaloy:
nitrogen can be in
Sponge ingot (Hafnium-free),
melt

Reprocessing



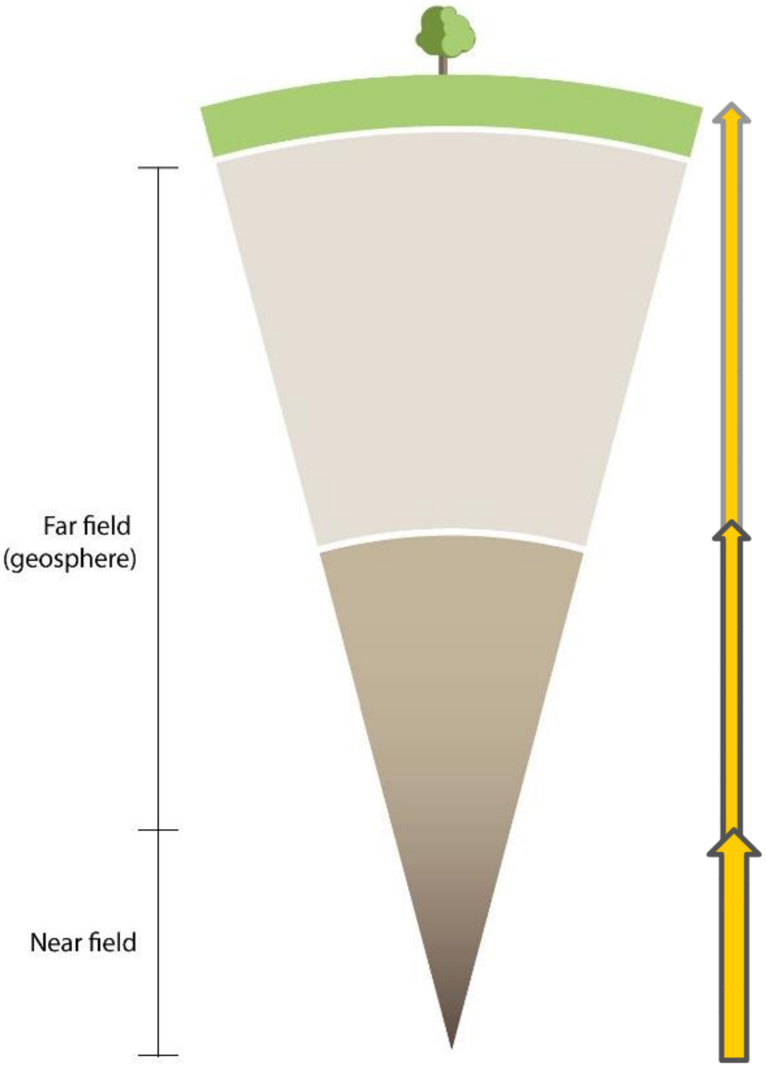
IAEA,2004

Geological disposal of waste



Water transport ($c_{chemical}$,∇,t) in natural evolution

Geological disposal of waste



Transport ($c_{chemical + radionuclides}$,$\nabla$,t) in natural evolution
Dissolved, gas
for example ^{14}C if CH_4 must be assumed

Transport ($c_{chemical + radionuclides}$,$\nabla$,t) in natural evolution
Dissolved, ionic
for example ^{129}I and ^{36}Cl and ^{14}C if HCO_3^- may be assumed

Transport ($c_{chemical + radionuclides}$,$\nabla$,t) in natural evolution
Retarded by sorption and ultrafiltration
for example complexes of actinides

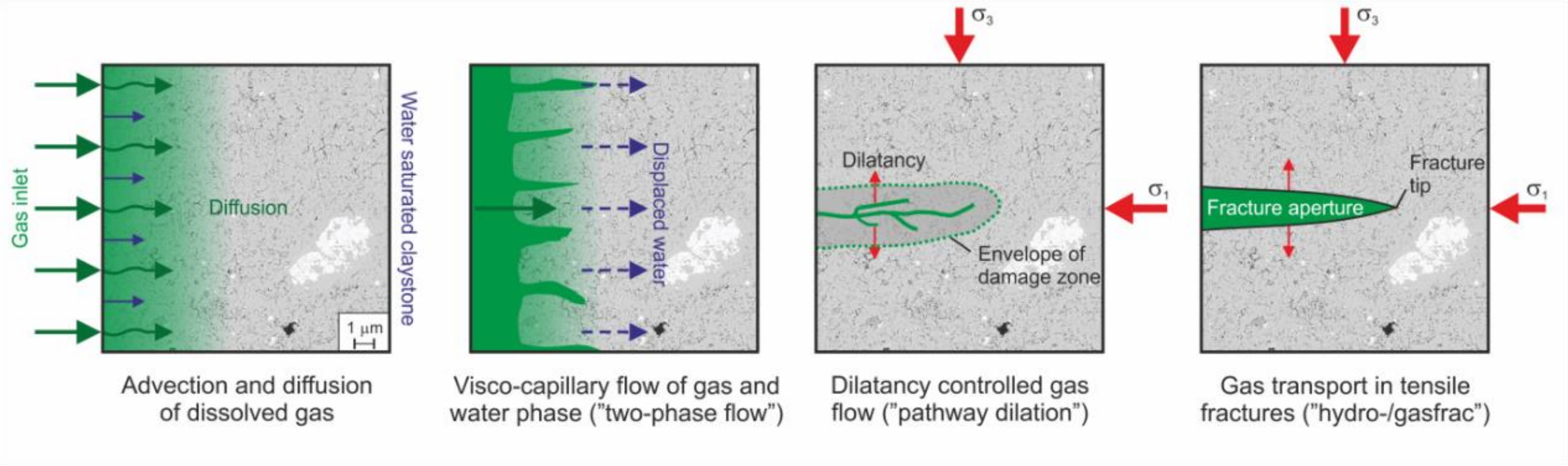
Gas, dissolved

- Waste types investigated in CAST
  - Neutron irradiated metallic compounds
    - Degradation: anaerobic corrosion
      - Hydrogen generation rate
  - Non-metallic neutron irradiated compounds

Free gas, dissolved gas

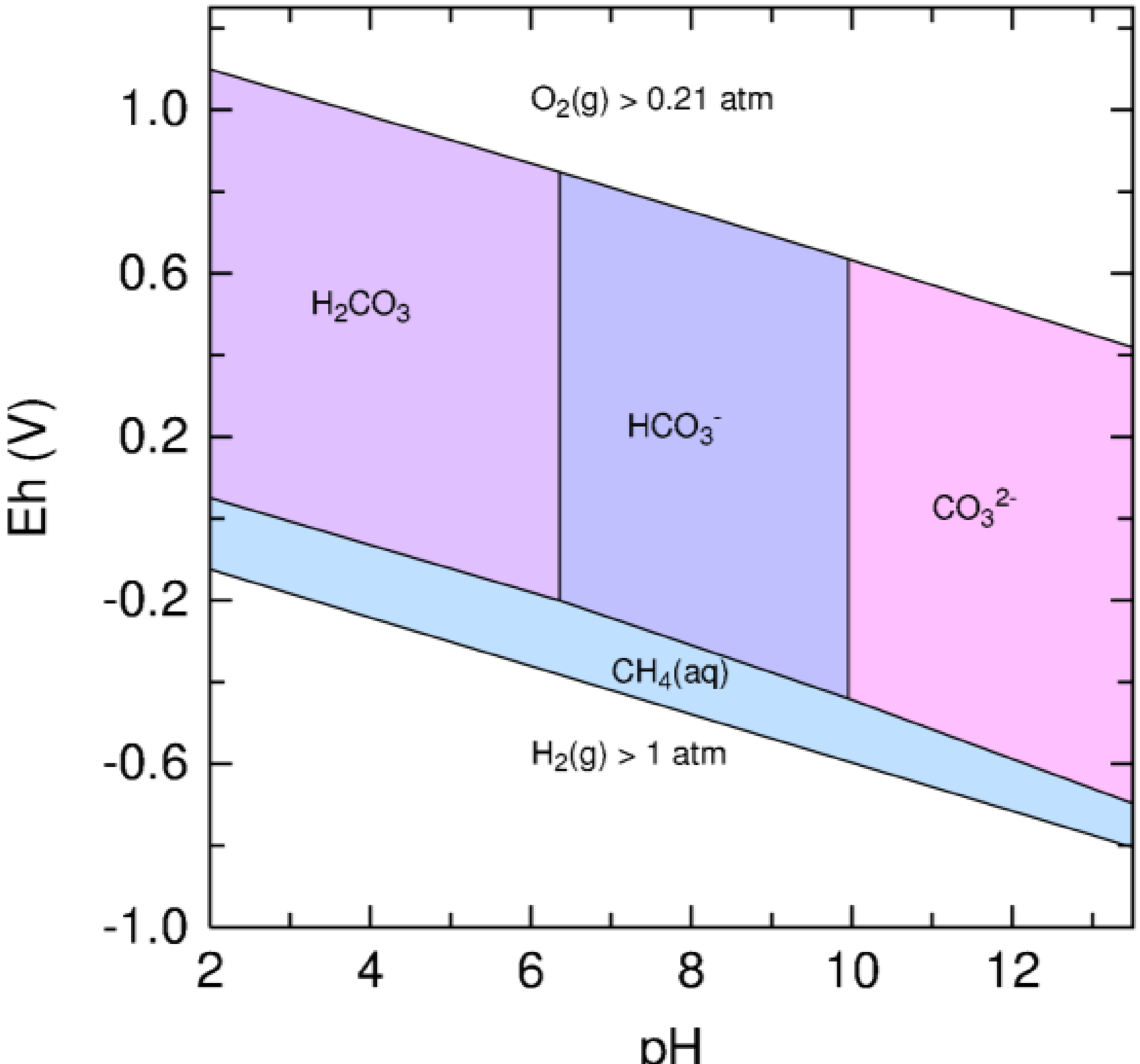
Identified in concrete?

yes yes yes



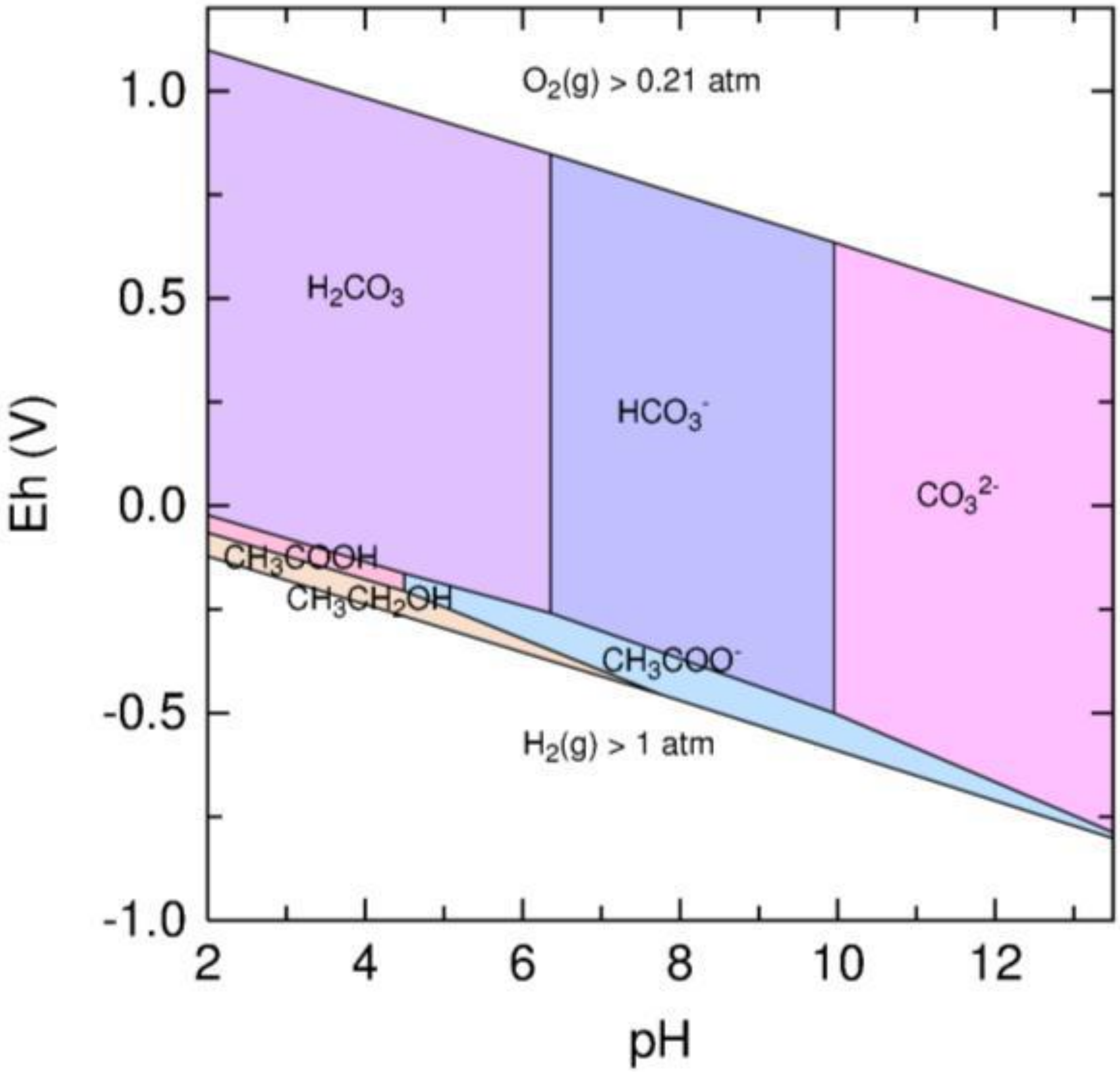
Wiseall, 2015

Gas, dissolved



Rizzato, 2015

Gas, dissolved



Rizzato,2015

Gas, dissolved

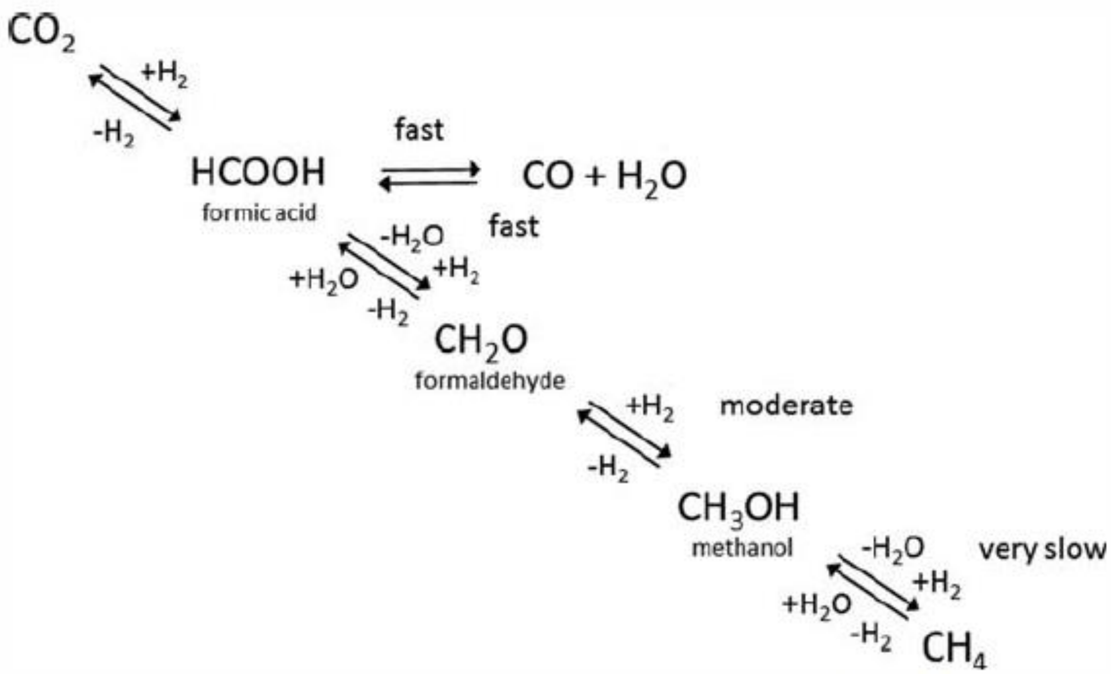
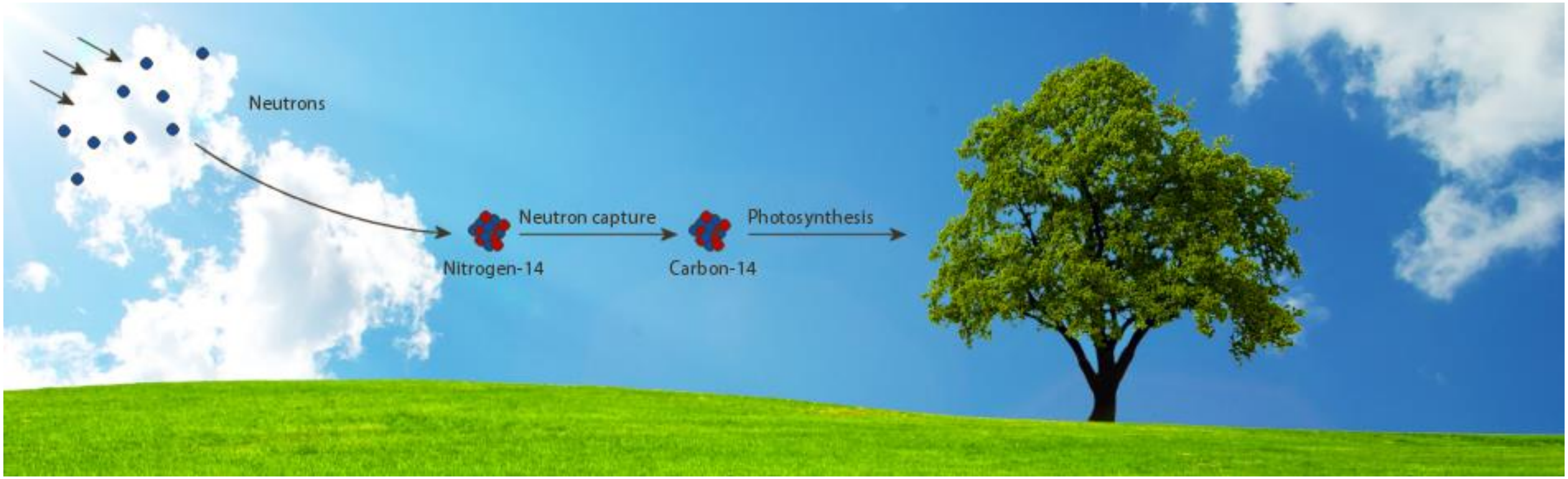


FIG. 4. Reaction scheme for the sequential reduction of CO_2 to methane (modified from McCollom and Seewald, 2007).

Wieland, 2015

Natural carbon-14



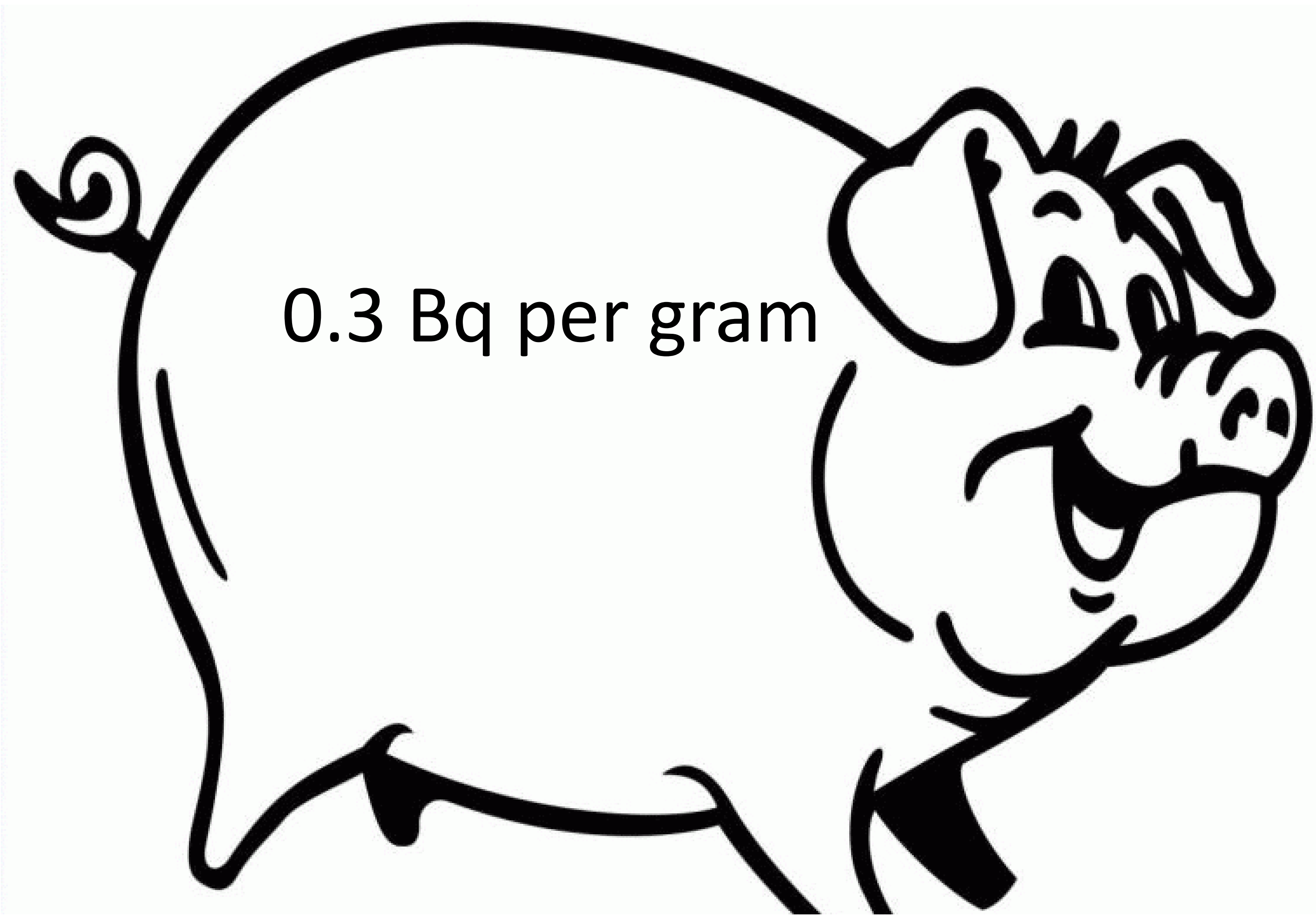
CAST project website home page & Newsletter 2

Exposure paths

- Inhalation
  - No concentration actor if not used by living matter for example noble gases
- Radiation exposure
  - For DTM radionuclides not likely
- Ingestion
  - Concentration actor if taken up by living matter for example carbon
    - Accumulation ^{14}C

IAEA, BIOMASS & ICRP,2012

Natural carbon-14



Main exposure path for humans: ingestion IRSN,2010

Potential artificial carbon-14

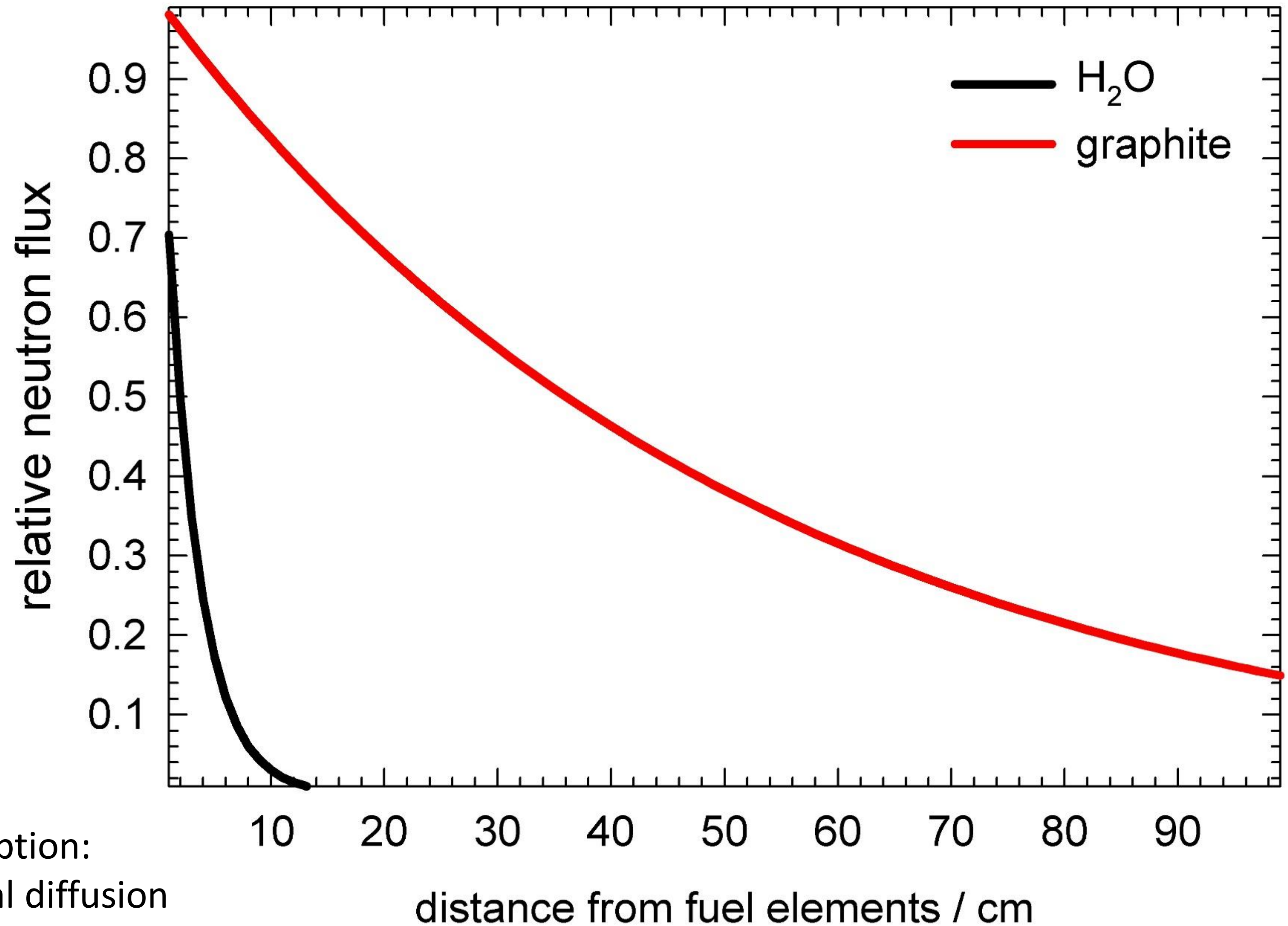
root zone, microbial oxidation

$^{14}CH_4$

Main exposure path: ingestion

BIOPROTA

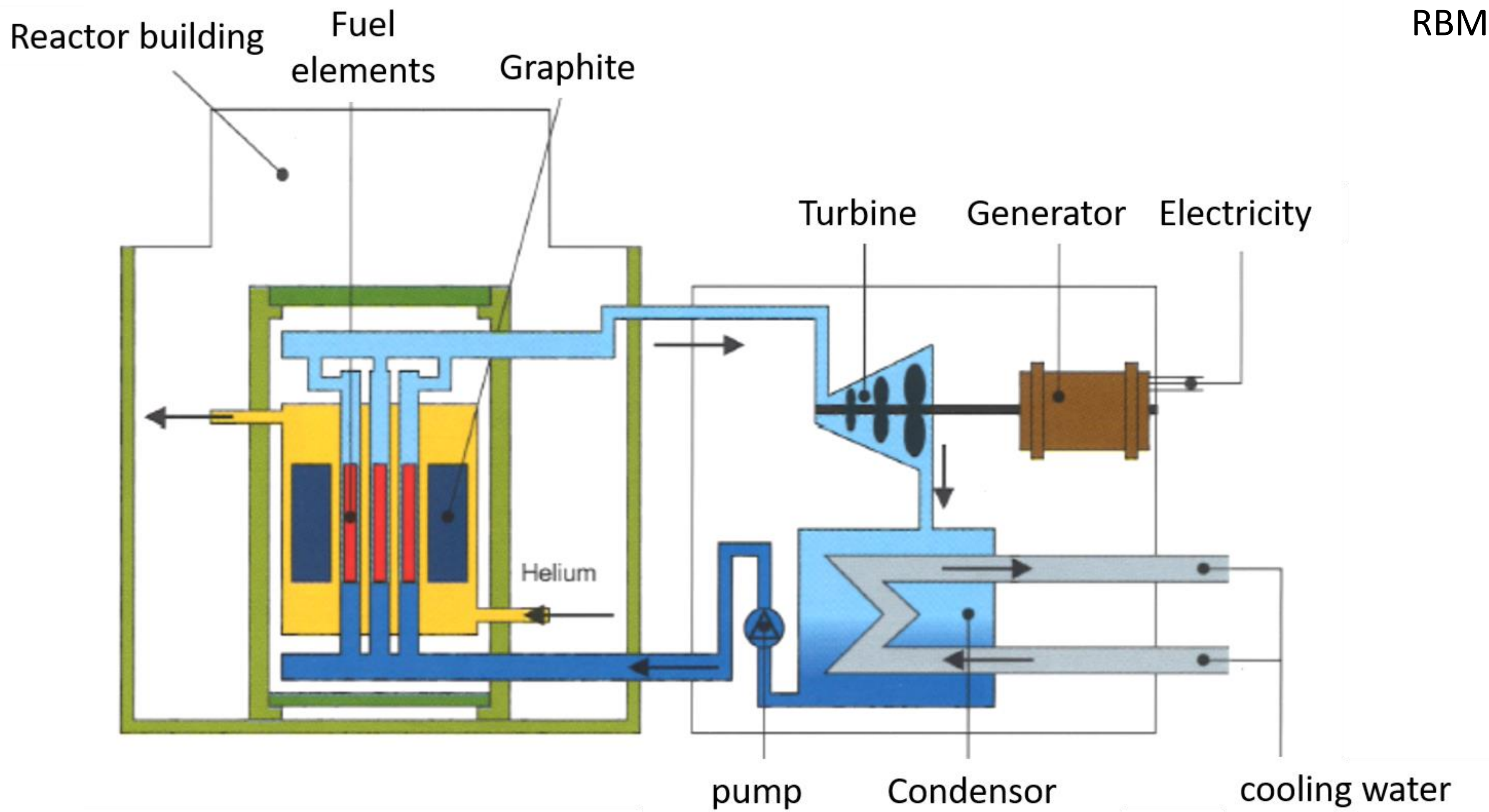
Generation



Assumption:
thermal diffusion

Generation

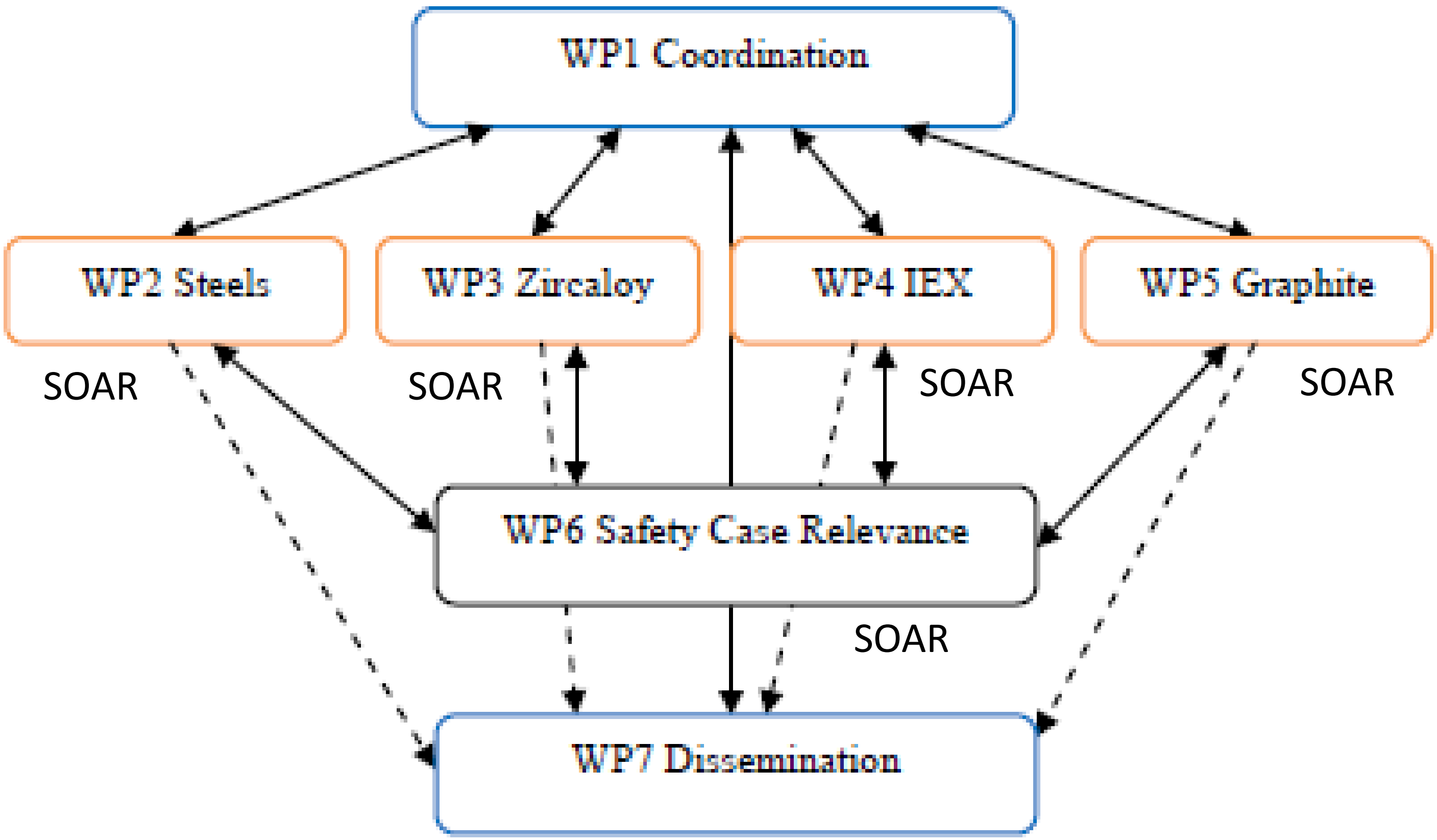
RBMK



Irradiated graphite, in CAST mainly LILW: moderator graphite instead of water
EU research project CarboWaste because HLW engineered barrier →
expected containment period several decay times of carbon-14 ($t_{1/2}$=5730 years)

Toulhout,2015

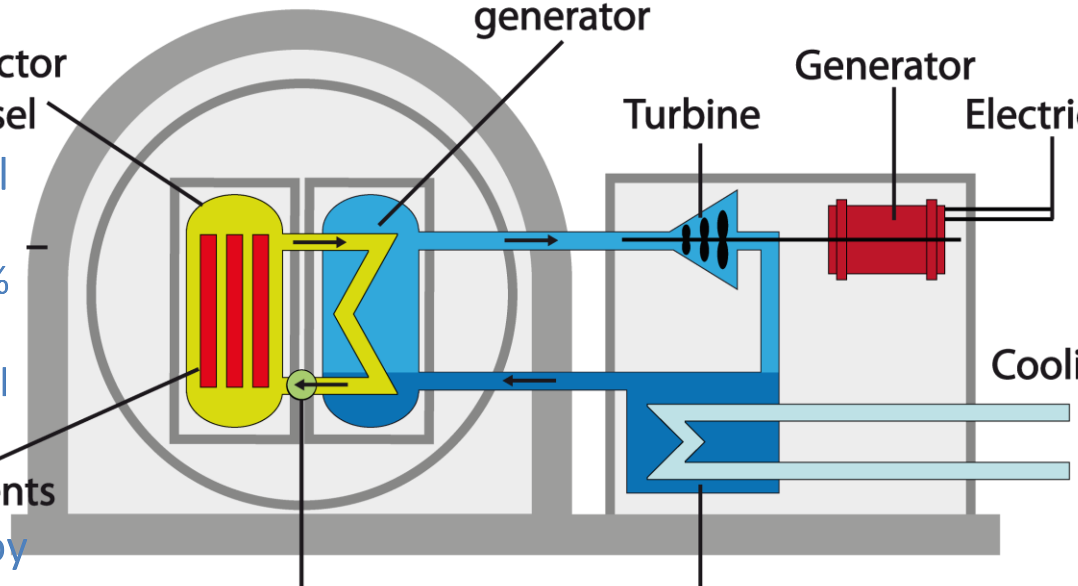
Carbon-14 Source Term



State Of the Art Report

Williams, Scourse: CAST project

Radiological characterisation



Irradiated steel

Corrosion resistance: stainless steel

Nitrogen stainless steel max 0.10 wt%

Core parts mainly activation

Minor contribution inner part vessel

Irradiated Zircaloy

Nitrogen 34 ± 10 ppm but unknown yet:

if LILW ⇨ reprocessing waste

1) mixture with (foreign) wastes
2) Inconel ends
3) additional contribution capture gaseous carbon-14

Spent ion-exchanger

Unknown yet:

oxygen-17 reduction in 10^3 cross section included

Irradiated graphite (in CAST mainly LILW):

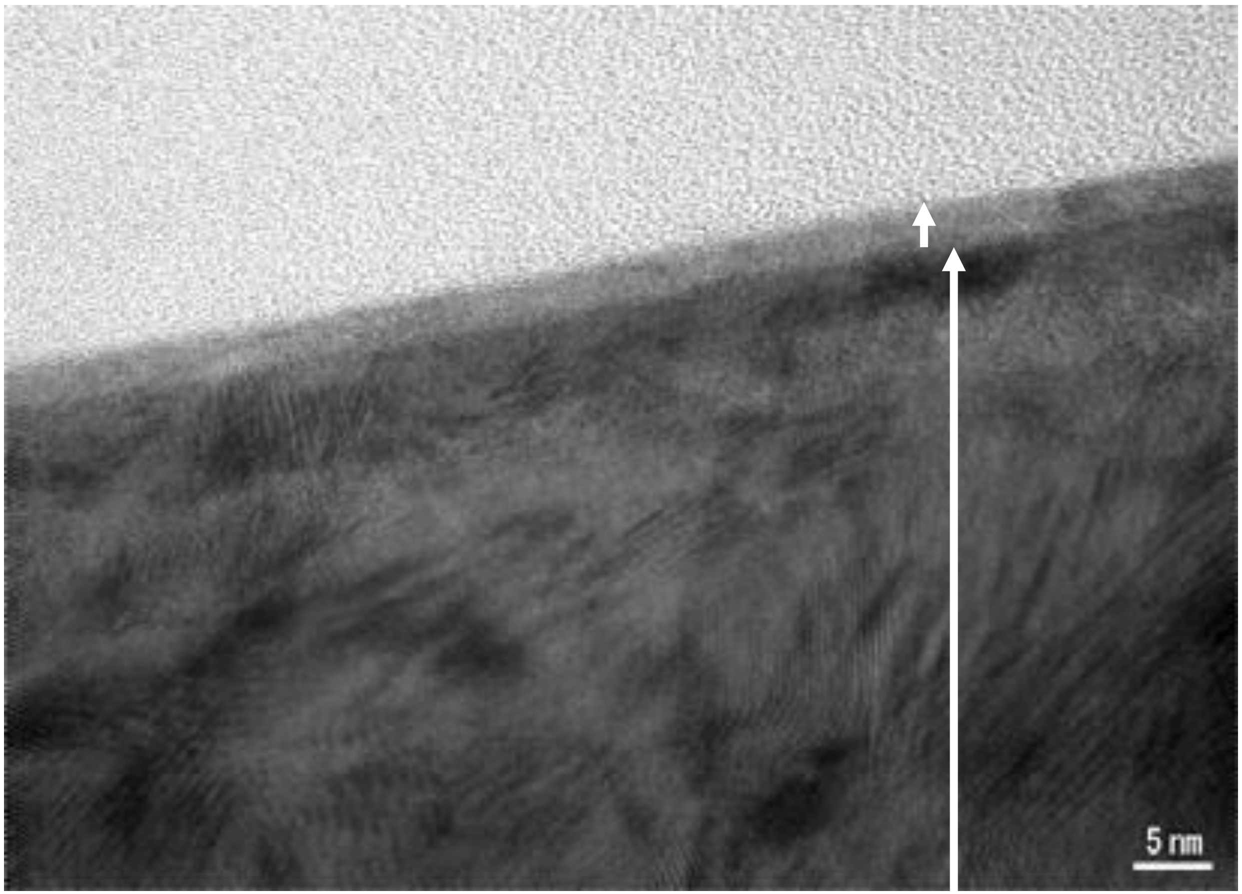
if nitrogen content larger than 15 ppm ⇨ main contribution to carbon-14

Neutron irradiated steel

- Core assumed 10^5 Bq per gram
- Outer parts for example vessel assumed 10^3 Bq per gram
  - Sample vessel available in CAST 18 Bq per gram steel

Mibus,2015 & Capouet, 2017

Neutron irradiated steel



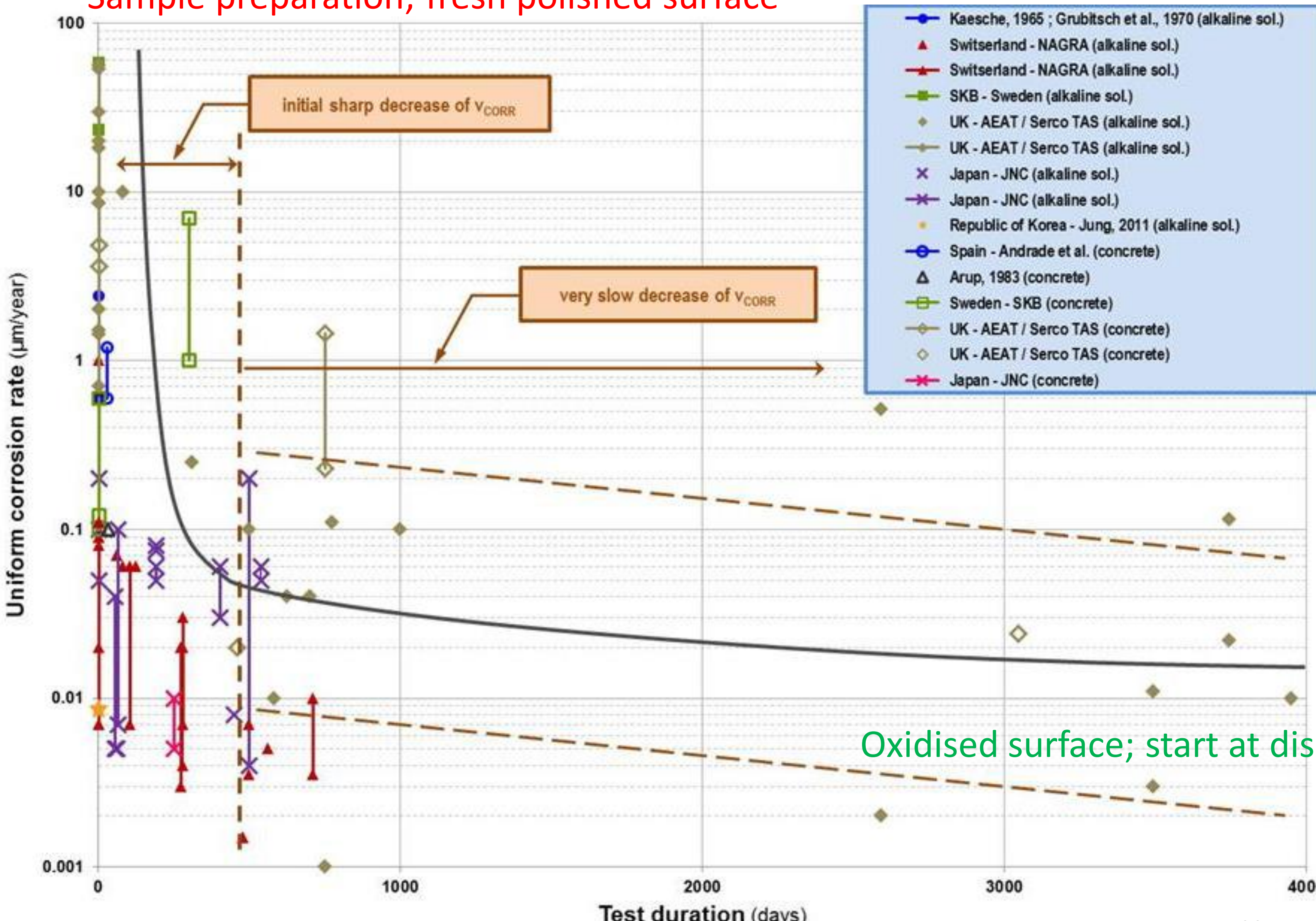
oxide

Metal

Mibus, 2015

Steel

Sample preparation; fresh polished surface



Oxidised surface; start at disposal

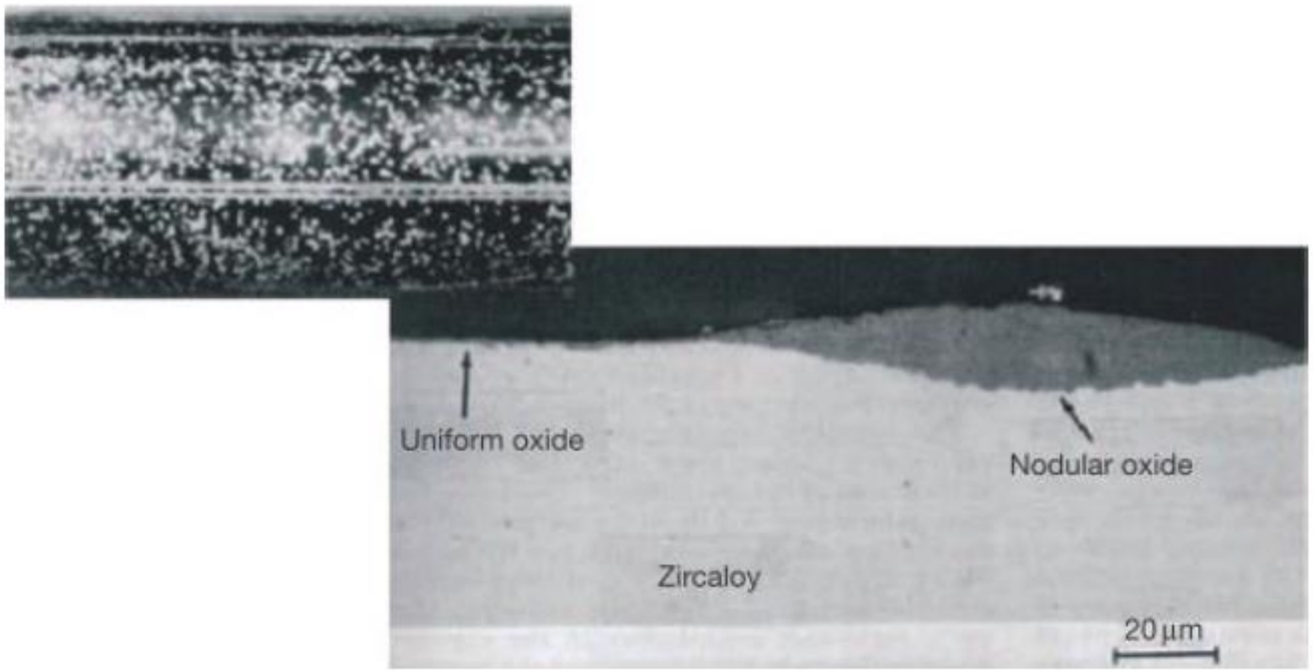
Kursten, 2015

Neutron irradiated Zircaloy

- ≈ 10^4 Bq ^{14}C per gram Zircaloy
  - Tenfold lower nitrogen content than steel
  - Operational waste not decommissioning waste consequently smaller neutron irradiation period
- Carbon solubility smaller than nitrogen solubility
  - Small precipitate 14-carbides

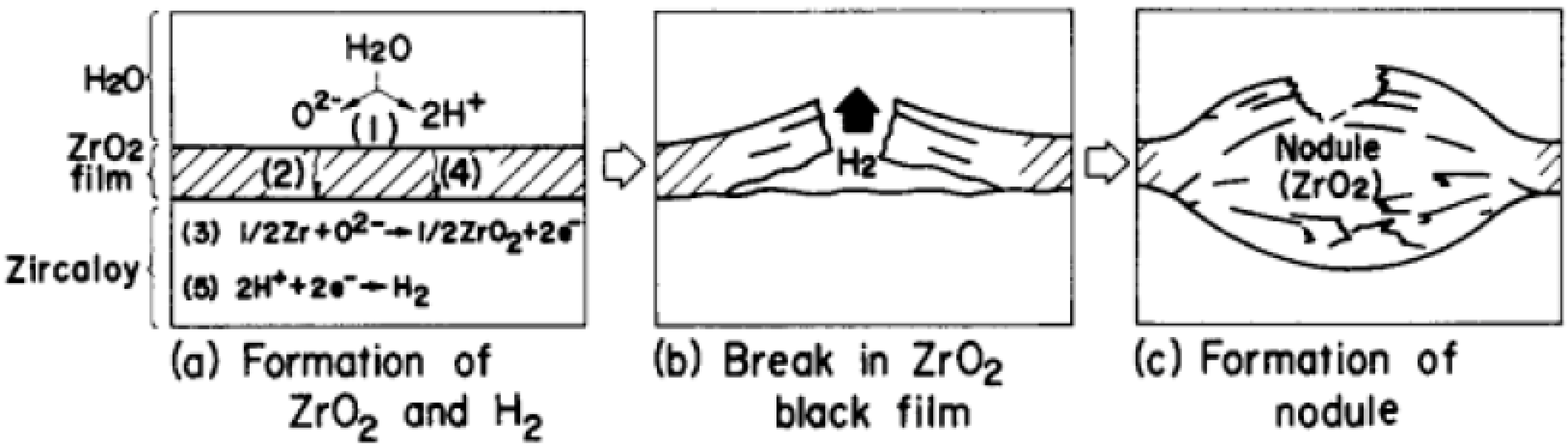
Gras, 2014

Neutron irradiated Zircaloy



Gras, 2014

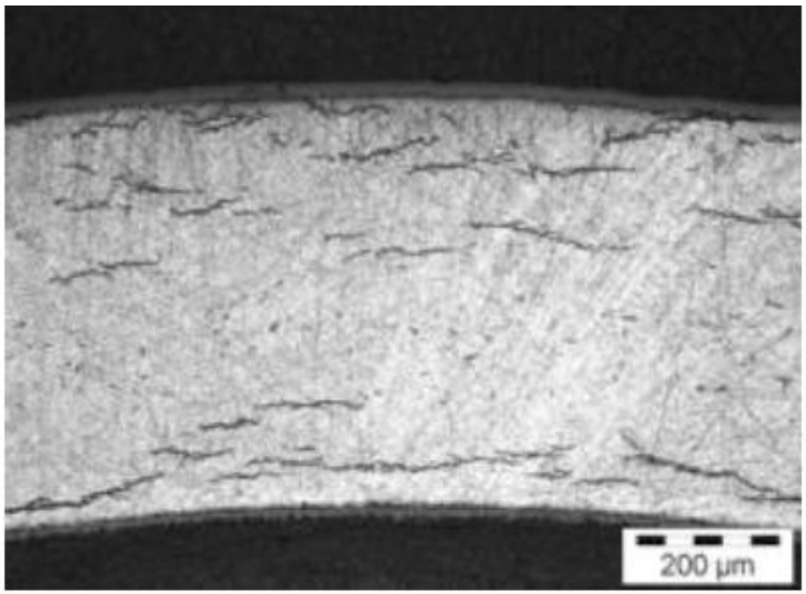
Neutron irradiated Zircaloy



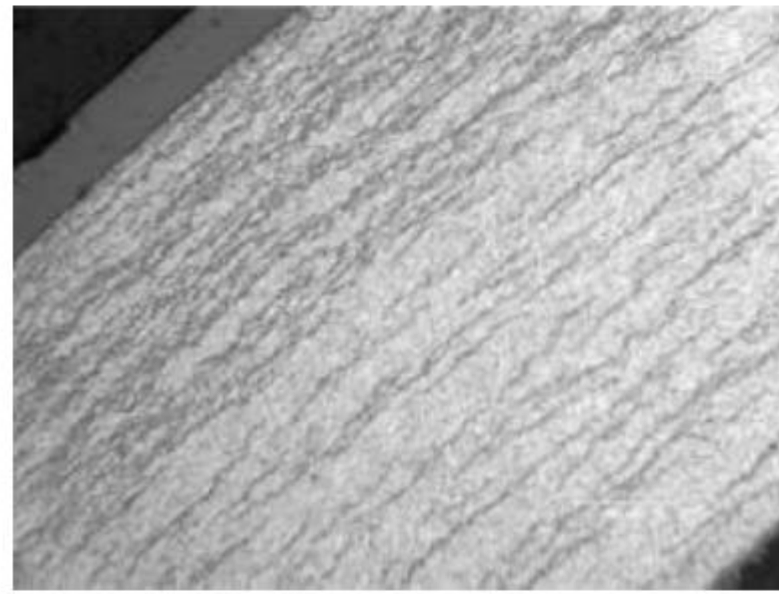
: Typical appearance of nodular corrosion in visual inspection and metallographic examination [ALL 2012] and mechanism of formation of lenticular nodules [KUW 1983]

Gras, 2014

Neutron irradiated Zircaloy



M5™, 5 cycles, stage 6
[AMB 2010]



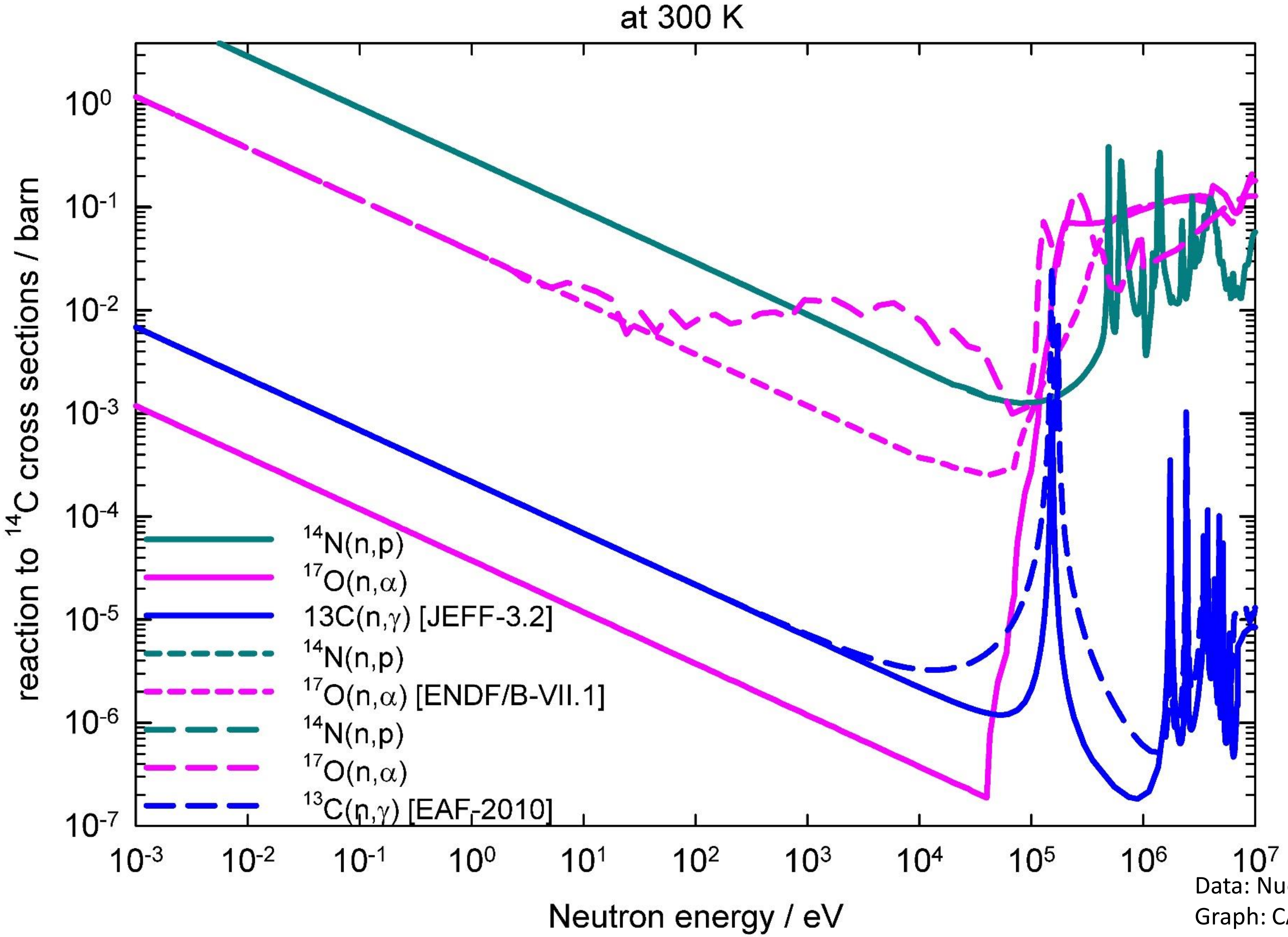
Zirlo™, 67 GWd.t^{-1}
[AND 2012]

Hydride formation

Gras, 2014

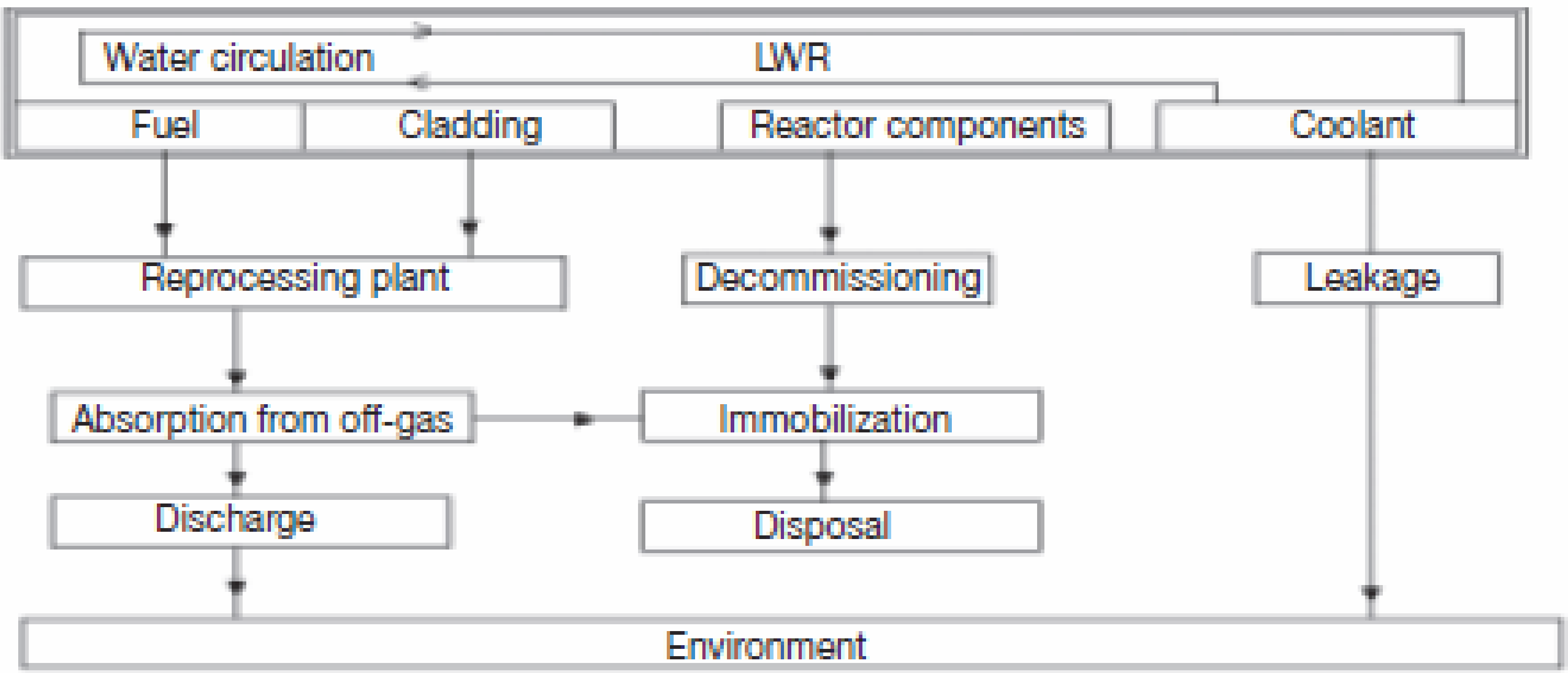
CSD-c as stored at COVRA's storage facility;
typical value for 900 MW NPP
1.4×10^{10} ^{14}C Bq per container
27000 Bq / gram solid waste
528 kg: 393 kg Zr (hulls) , 19 kg Inconel (ends) , 116 kg ss (technological waste)
Reported by AREVA

Spent ion exchange resins



Data: Nuclear Energy Agency
Graph: CAST Newsletter 2

Spent ion exchange resins



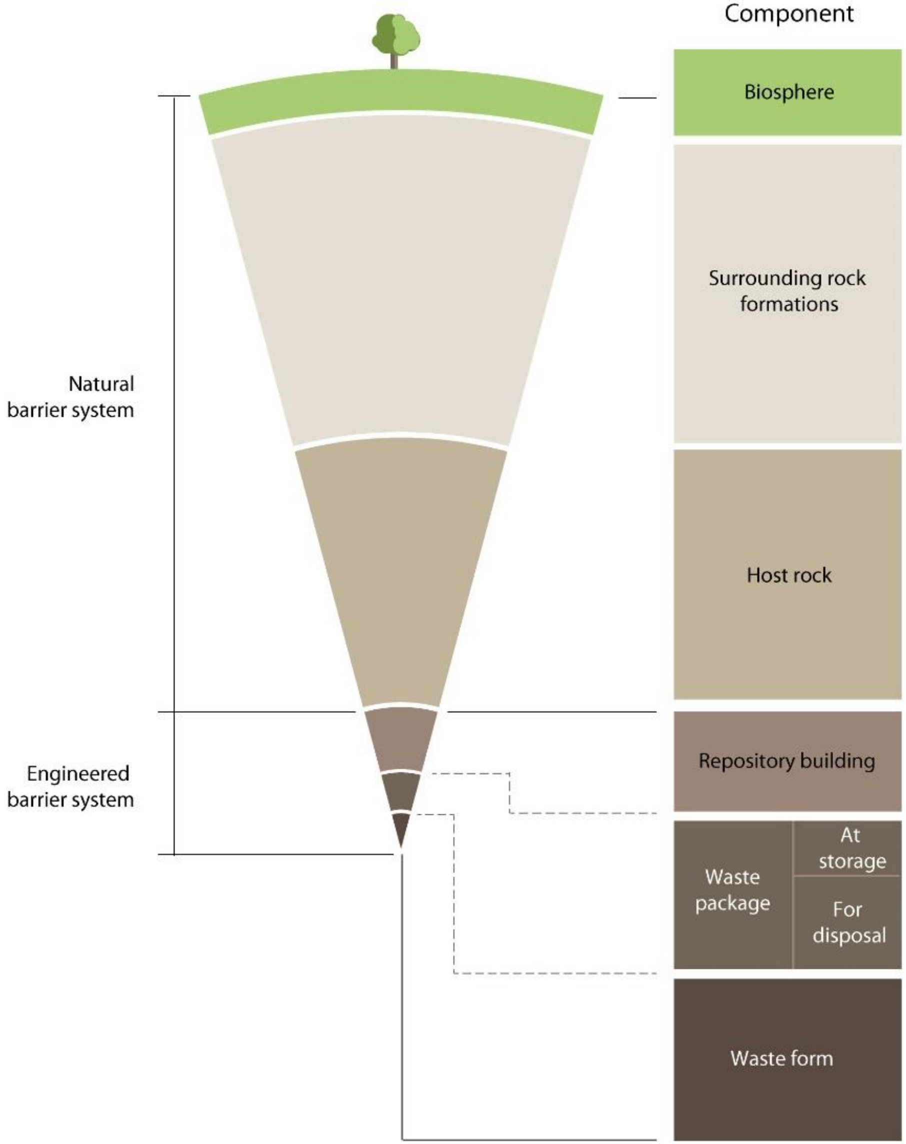
IAEA,2004

Neutron irradiated graphite

- Romania: contact-handled irradiated graphite
  - see first CAST Newsletter

- Italy: remote-handled irradiated graphite
  - Canzone G et al (SOGIN) Dismantling of the graphite pile of Latina NPP: Characterization and handling/removal equipment for single brick or multi-bricks, Progress in Nuclear Energy 93 (2016) 146-154

Release mechanism

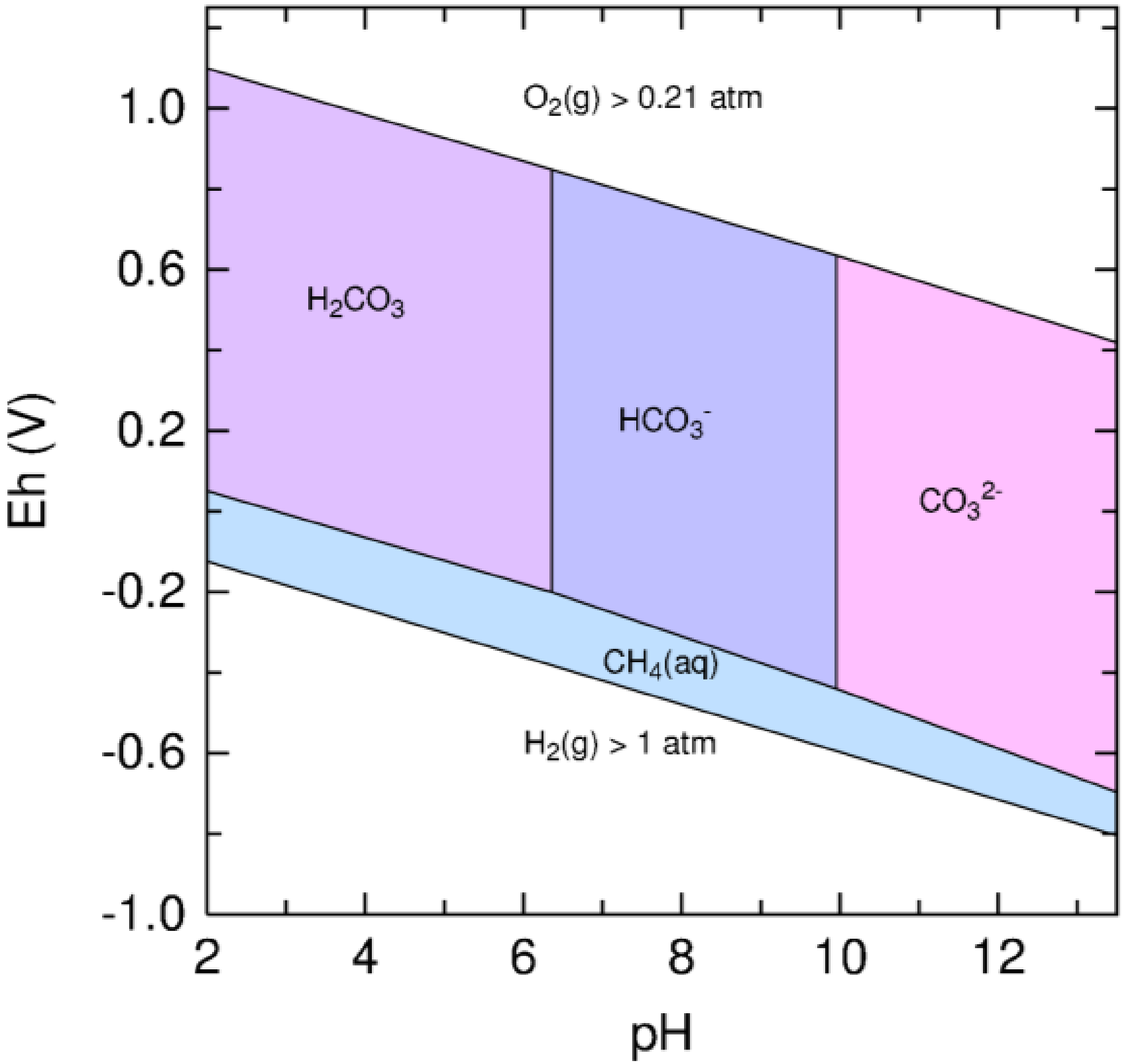


Cementitious materials

Release mechanism

- Source term: carbon-14 release rate or rates from waste
- Release under conditions relevant for waste packaging and disposal to underground facilities
  - Cementitious matrices, main waste packaging conditions considered in CAST
  - Cement alkaline conditions
    - Portland: initially slightly oxidising and largely unbuffered because of lack of electroactive species
      - corrosion of metals may reduce redox potential locally
    - Blast furnace slag: initially reducing due small amount of FeS_2 – blueish colour when not oxidised –
      - corrosion of metals may locally sustain reducing conditions
  - Underground
    - Near-surface disposal: aerobic exposure conditions
    - Deep geological disposal: anaerobic exposure conditions

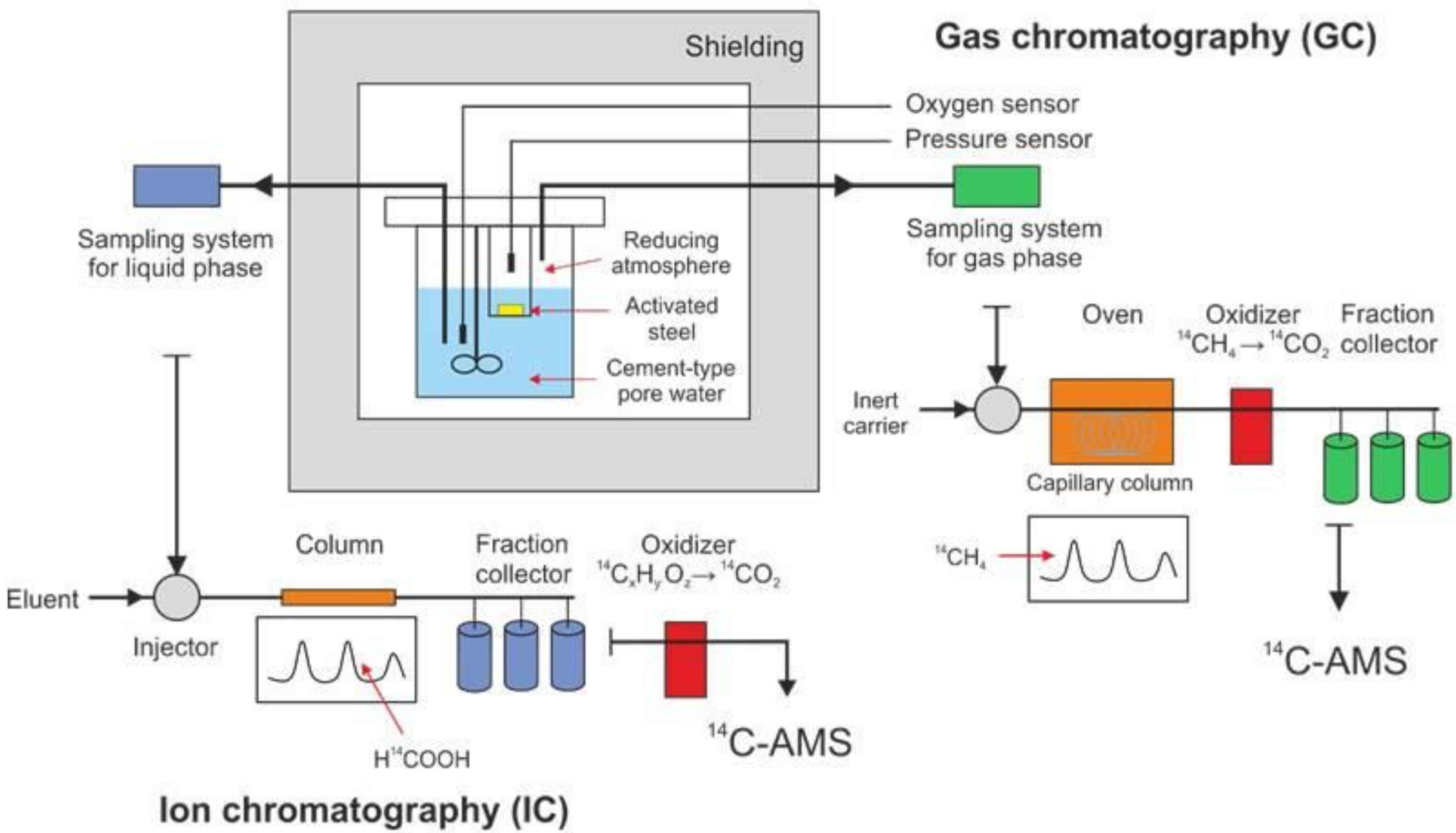
Speciation



Surface disposal
maybe not if metals

Geological disposal
BFS cement

Speciation measurement



Wieland, 2017

Conclusions / highlights

- CAST finishes on 1 April 2018
  - Final General Assembly Meeting in January 2018 in France (Lyon)
    - Submission abstracts before 1 September 2017
- During running research programme CAST
  - State Of the Art reports at start of the programme
    - knowledge management
    - End-User view: what does experimental research contribute to what is already known?
  - Determination activity concentration of carbon-14 in waste appeared to become more important
    - Nitrogen impurities in steel measured
      - Unknown if nitrogen content has been reduced since 1984 ALARA
    - Main presence carbon-14 in processed waste, in Zircaloy hulls, not yet known
    - Focus on reliable determination of carbon-14 activity concentration in spent ion exchange resins, speciation of ionic carbon not yet identified
    - Also in neutron irradiated graphite, nitrogen impurities can be main source of carbon-14
  - Obtaining representative samples and setting-up experiments takes time
    - Corrosion rates of steel at geological disposal, i.e. passivated surfaces in cementitious materials, perhaps too hard to measure reliably DTM radionuclide carbon-14 release rate
    - Nitrogen at impurity level expected to be dissolved in metal lattice consequently congruent release of carbon-14 may be expected if migration of carbon within steel at reactor conditions can be neglected

Plan of content training course

- Like PETRUS-ANNETTE free of charge
  - Have a look at www.projectcast.eu/training/courses for further details
- Plan of content
  - For the types of waste investigated in CAST
    - Generation of carbon-14 in nuclear plant
    - Calculate potential release of radionuclides
  - Scheduled at the end of 2017 / early 2018
    - probably in the Netherlands in order to visit the waste investigated in CAST
    - About two days
  - Please send an e-mail to erika.neeft@covra.nl if you are interested preferably after your summer holiday

Thank your for attention
any questions?

References

CAST reports and newsletters free online available at www.projectcast.eu

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